

CHARACTERIZATION OF MULTIBLOCK COPOLYMERS BY CHROMATOGRAPHY METHODS

Vom Fachbereich Chemie
der Technischen Universität Darmstadt

zur Erlangung des akademischen Grades eines

Doktor rerum naturalium
(Dr.rer.nat)

genehmigte Dissertation

vorgelegt von

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Tag der Einreichung:	03.12.2009
Tag der mündlichen Prüfung:	08.02.2010

Darmstadt 2010

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I thank the Almighty and Saviour, The Lord Jesus Christ, for the support during my struggle time.

I would like to express my gratitude to all the people who played an active role in the achievement of this PhD thesis. I thank Prof. Harald Pasch who gave me the opportunity to work in his group and who devoted me a lot of his time during my stay at DKI.

I would also like to thank Dr. Wolfgang Radke for his assistance, advice and valuable contributions made towards this interesting and challenging research. His experience represented always high quality inputs to this PhD. His sense of humour will be missed.

I am very grateful to Deutscher Akademischer Austausch Dienst (DAAD) for the financial support.

I am also grateful to all my past and present colleagues of DKI who made my stay at the institute so pleasant. I appreciate the friendly atmosphere during the work as well as during the leisure activities. Thank you for having made me feel more than welcome in Germany.

A special thank you goes to Achille Bivigou Koumba and Isabel Haamel. They have always been there for me during the difficulties and troubles times I encountered throughout this study.

Big thank goes to my friends outside the institute. I personally want to mention Yann Moupinda, Regis Ngoma, Romual Itomba, Ivan Mikomba, Yannick Affogolo, Come Ngouele, Ghislain Talani, and Stephane Ibinga

Enfin je remercie tous mes parents qui m'ont aidé, soutenu et encouragé dans mes études, à qui je souhaite exprimer toute ma tendresse et l'immense joie qui m'habite lorsque je suis avec eux.

Diese Arbeit wurde am Deutschen Kunststoff-Institut unter Leitung von Prof. Dr. H. Pasch in der Zeit von Februar 2006 bis December 2009 durchgeführt.

Je dédis cette thèse de doctorat à tous ceux, qui m'ont soutenu de près ou de loin, d'une manière ou d'une autre au nom du Tout Puissant Seigneur Jésus Christ.

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German Summary

Das Interesse und die Forderung nach innovativen Produkten mit neuen Eigenschaften resultiert in der Entwicklung einer großen Vielzahl neuer komplexer Polymermaterialien. Dies führt zu einer erhöhten Nachfrage nach geeigneten Charakterisierungsmethoden, um die molekulare Struktur dieser Materialien zu verstehen und mit den makroskopisch messbaren Eigenschaften verknüpfen zu können, woraus sich schließlich Struktur-Eigenschaftsbeziehungen ableiten lassen. Deren Kenntnis erlaubt die Optimierung der Syntheseparameter und damit der resultierenden Gebrauchseigenschaften.

Das Ziel der vorliegenden Arbeit war es daher analytische Methoden zu erarbeiten, um die Funktionalitätsverteilung (FTD) von Poly(p-dionanon)- (PPDO) und Poly(caprolactone)-diolen (PCL) aufzuklären. Weiterhin sollten Informationen zur chemischen Heterogenität von Multiblockcopolymeren (MBC), die durch Verknüpfung der beiden genannten Polyesterdiolen mit Diisocyanaten erhalten wurden, gewonnen werden.

Zunächst wurden chromatographische Bedingungen erarbeitet, die eine Trennung der PPDO- und PCL-Diolproben nach der Anzahl der OH-Endgruppen ermöglichen. Für PCL wurden hierzu auf einer polaren stationären Phase die kritische Eluentenzusammensetzung zu 92% Dichlormethan (DCM) und 8% Tetrahydrofuran (THF) bestimmt. Für alle PCL-Diole wurden unter diesen Bedingungen zwei Peaks erhalten. Der erste Peak eluierte nahe dem Totvolumen der Säule und wurde PCLs ohne polare OH-Gruppen zugeordnet. Der zweite Peak eluierte bei höherem Elutionsvolumen, bedingt durch die zusätzliche Retention zweier OH-Gruppen mit der stationären Phase. Obwohl unter kritischen Bedingungen gearbeitet wurde, eluierten die Diole in der Reihenfolge abnehmender Molekulargewichte. Der Grund hierfür kann darin gesehen werden, dass bei hohen Molekulargewichten die beiden OH-Gruppen statistisch unabhängig voneinander adsorbiert werden. Bei kurzen Polymerketten hingegen adsorbieren die OH-Gruppen nicht mehr unabhängig voneinander. Sobald die erste OH-Gruppe adsorbiert ist, befindet sich auch die zweite OH-Gruppe in der Nähe der Oberfläche der stationären Phase. Hierdurch wird

die Wahrscheinlichkeit für die Adsorption erhöht, was zu längeren Retentionszeiten führt.

Ein 10 minütiger linearer Gradient von 100% DCM nach 100% Dimethylformamid (DMF) wurde auf einer polaren stationären Phase verwendet, um PPDOs nach ihren Endgruppen zu trennen. Unter den gewählten chromatographischen Bedingungen zeigten die PPDO-Diolproben zwei Peaks. Die Charakterisierung der Fraktionen mittels MALDI-TOF-MS (Matrix Assisted Laser Desorption Ionisation Time Of Flight Mass Spectrometry) zeigten, dass der erste Peak hauptsächlich PPDO-Ketten mit zwei OH endgruppen enthielt. Die MALDI-TOF-Spektren des zweiten Peaks wiesen drei unterschiedliche Serien auf. Die Massen dieser Serien waren in Einklang mit der Annahme zyklischer PPDOs sowie Ketten mit je einer Carboxyl- und einer OH- bzw. einer Li-Carboxylat- und einer OH endgruppe.

Um Informationen zur chemischen Heterogenität der MBC-Proben zu erhalten, wurde eine Gradientenmethode entwickelt. Diese erlaubt die Trennung von PPDO-Diolen und PPDO-Multiblockpolymeren (MBP) von PCL-Diolen und PCL-MBP. MBP sind dabei definiert als Polymere die durch die Verknüpfung von entweder PCL- oder PPDO-Diolen mit Diisocyanaten enthalten werden. Die Anwendung des entwickelten Gradientenverfahrens auf die MBC-Proben ergab jeweils zwei gut getrennte Peaks. Der erste der Peak eluierte dabei im SEC-Modus, vor Beginn des Gradienten im Elutionsbereich von PPDO-Diolen und PPDO-MBP. Da der bei Gradientenstart verwendete Eluent eine Adsorption der PCL-Einheiten bewirkt, lässt sich aus den Retentionszeiten des ersten Peaks auf das Vorliegen rein PPDO-haltiger Strukturen schließen. Der zweite Peak zeigte ähnlichen Retentionszeiten wie die PCL-Diole und die PCL-MBP. In der Gradientenchromatographie werden die Retentionszeiten von Blockcopolymeren im Wesentlichen durch die chemische Struktur des adsorbierten Blockes bestimmt. Daher eluieren Homopolymere mit der gleichen chemischen Struktur wie der adsorbierende Block eines Blockcopolymeren bei ähnlichen Retentionsvolumen, wie das Blockcopolymer. Somit kann aus den Retentionszeiten der Gradientenchromatographie gefolgert werden, dass der zweite Peak PCL-Einheiten aufweist. Somit kann er aus PCL-Diolen, PCL-MBP oder MBC resultieren.

Zur Klärung der Frage, ob der zweite Peak der Gradientenchromatographie echte Copolymerstrukturen enthält oder nur aus PCL aufgebauten Strukturen (Diole und MBP) wurde die Flüssigkeitschromatographie unter den kritischen Bedingungen der Adsorption (LCCC) angewandt. Auf einer Umkehrphase wurden zunächst die kritischen Bedingungen für PCL ermittelt (76% Acetonitril (ACN), 24% Dichlormethan (DCM)). Unter diesen Bedingungen erwartet man für Strukturen, die PPDO enthalten eine Elution vor dem Totvolumen der Säule, während für nur PCL-haltige Ketten eine Elution am Totvolumen der Säule erwartet wird. Die Messung der MBC-Proben unter den genannten Bedingungen ergab zwei Peaks für alle Proben. Basierend auf den Retentionszeiten kann für den ersten Peak vermutet werden, dass er durch PPDO-haltige Strukturen (Diole, PPDO-MBP, MBC) hervorgerufen wird. Der zweite Peak eluierte am Totvolumen der Säule, ebenso wie PCL-Diole und PCL-MBP. Daher kann dieser Peak "reinen" PCLs und/oder PCL-MBP zugeordnet werden.

Anhand der chromatographischen Untersuchungen kann somit gefolgert werden, dass die MBC-Proben sowohl signifikante Anteile an nur PPDO-haltigen (Gradientenchromatographie) als auch nur PCL-haltigen (LCCC) Strukturen aufweisen. Es ist jedoch anhand der chromatographischen Ergebnisse nicht möglich, die Existenz von MBC auszuschließen, da diese in beiden chromatographischen Experimenten mit MBP oder Diolen coeluierten sollten.

Um die gemachten Zuordnungen weiter zu verifizieren und um herauszufinden, ob auch MBC-Strukturen vorliegen, wurden die Peaks der Gradientenchromatographie off-line mittels Fourier Transform Infrarot-Spektroskopie (FTIR) untersucht. Dabei zeigte das FTIR-Spektrum des ersten Peaks die charakteristischen Absorptionsbanden von PPDO, während die für PCL charakteristischen Absorptionen nicht auftraten. Dies belegt das Vorliegen von rein PPDO-haltigen Strukturen. Das FTIR-Spektrum des zweiten Peaks hingegen zeigte die charakteristischen Banden von PCL, ohne jedoch die charakteristischen Banden des PPDO aufzuweisen. Dies lässt vermuten, dass die zweite Fraktion in der Gradientenchromatographie nahezu vollständig aus PCL-Einheiten besteht. Diese Ergebnisse bestätigen somit die anhand der Retentionszeiten gemachten Zuordnungen. Weiterhin belegen die FTIR-Ergebnisse,

dass die MBC-Proben sich aus reinen PPDO-haltigen- bzw. reinen PCL-haltigen Ketten zusammensetzen, ohne dass PPDO und PCL als MBC in der gleichen Kette vorliegen. Es scheint sich somit um Mischungen aus PPDO-MBP und PCL-MBP zu handeln.

Diese sehr unerwarteten Resultate sollten durch weitere Untersuchungen abgesichert werden. Daher wurde die Pyrolyse mit gekoppelter Gaschromatographie/Massenspektrometrie (Py-GC-MS) als alternative Methode zur FTIR eingesetzt. Die Gradientenchromatographie wurde verwendet, um die beiden Peaks in zwei Fraktionen zu trennen. Diese Fraktionen wurden anschließend mittels PY-GC-MS untersucht. Die quantitativen Untersuchungen zeigten, dass die erste Fraktion der MBC, die dem ersten Peak der Gradientenchromatographie entspricht, zu mehr als 80 % aus PPDO besteht, wogegen in der zweiten Fraktion nur bis zu 10 % PPDO gefunden wurde.

Die Ergebnisse der FTIR- und der Py-GC-MS sind qualitativ in guter Übereinstimmung, belegen Sie doch, dass die beiden Peaks sich in ihren Zusammensetzungen deutlich unterscheiden. In den quantitativen Ergebnissen hingegen unterscheiden sie sich, da die FTIR-Spektroskopie jeweils nur eine Polyesterkomponente pro Peak identifizieren konnte, während die Py-GC-MS die in jedem chromatographischen Peak jeweils beide andere Polyesterkomponenten, wenn auch mit sehr unterschiedlichen Anteilen nachweisen konnte.

Weitere Charakterisierungen der beiden Fraktionen der MBC wurden mittels ^1H -NMR-Spektroskopie (^1H -NMR) durchgeführt. Die quantitative Auswertung der Spektren für die Fraktionen zeigte, dass die erste Fraktion mehr als 80% PPDO enthält, die zweite hingegen nur etwa 20%. Diese Ergebnisse sind daher in guter Übereinstimmung mit denen der Py-GC-MS.

Aus den durchgeführten Untersuchungen konnte somit geschlossen werden, dass die untersuchten MBC bezüglich ihrer chemischen Zusammensetzung unerwartet heterogen sind. Diese Ergebnisse waren sehr wertvoll, da sie erlaubten die Synthesebedingungen so zu verändern, dass Proben mit erheblich geringerer chemischer Heterogenität resultierten.

1. Introduction

Shape memory materials (SMMs) are materials, including shape memory alloys (SMAs), ceramics and polymers (SMPs) which are termed intelligent or adaptive materials. Shape memory materials have been used for some time in the past and a variety of engineering and biomedical applications are based on shape memory alloys and ceramics already today [1-3,30,35]. In comparison to these materials shape memory polymers, which have been developed in the last decade, are lagging behind despite their many novel advantageous properties, e.g. maximum recoverable strain up to 400% [4-5,30], very high shape recoverability, low density, low cost, easy shape programming, easy control of recovery temperature and the possibility to adjust color. In contrast to other shape memory materials, the shape memory effect of shape memory polymers can be triggered by various external stimuli, other than heat, such as light or pH change. This allows for innovative usage in new fields of application. Due to the different stimuli that can be used to trigger the shape memory effect, SMPs are categorized into three types, namely, thermal-responsive SMPs, photo-responsive SMPs and chemo-responsive SMPs [1,6,30]. Among them, the thermo-responsive SMPs have been the major focus of investigation in the past years and some products utilizing their properties are commercially available at present.

The actual shape memory effect (SME) consists of a thermo-mechanical cycle and is schematically illustrated in Fig. 1.1[91]. The raw material is simply processed into a pre-determined shape (the original or permanent shape) by molding, heating, casting or coating. In the next step the SMP is deformed into its temporary shape at an elevated temperature (programming temperature). The load is maintained during cooling to maintain the temporary shape (a). After cooling the removal of the load results in a very small elastic shape recovery, but the deformed shape is largely maintained (b). The deformed shape is stable until shape recovery triggered by an external stimulus (e.g. heating). Upon activation by reheating the SMPs to or above the programming temperature, the material adopts its original or permanent form without any additional mechanical action (c). This SME cycle is repeatable.

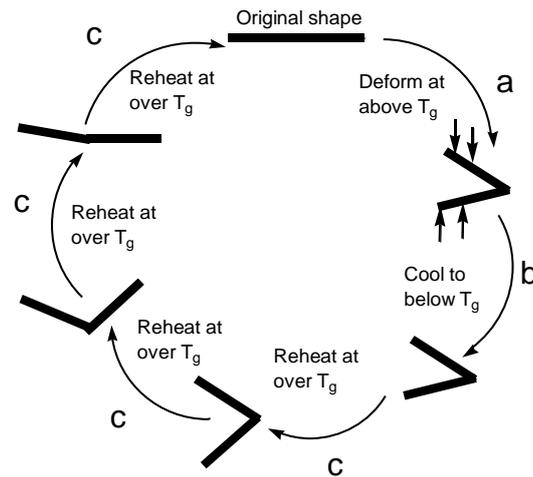


Figure 1.1: Illustration of SME

The shape memory effect is not an intrinsic material property, but is a consequence of a combination of phase morphology and processing technology. Shape memory polymers are usually composed of segmented copolymers consisting of crystalline or high T_g segments (hard segment) as well as amorphous segments of lower T_g (soft segment). Therefore SMPs usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard, rigid segments segregate into a glassy or semicrystalline domain, while the soft segments form amorphous or rubbery matrices in which the hard segments are dispersed. The hard domain in this two-phase microstructure acts as physical crosslinks, while the soft segment behaves as a soft matrix. This microphase separation results in superior physical and mechanical properties, such as high modulus and high reversible deformation. The degree of phase separation or domain formation not only depends on the weight ratio of the hard to the soft segment, but also on the type and molar mass of the segments, the manufacturing process and reaction conditions [7-11].

At the molecular level the mechanism of the SME of SMP can be explained by examining their microstructures. Hard and soft segments are usually thermodynamically immiscible, so that microphase separation of the segments occurs. In the relaxed state after processing the polymer into its permanent shape, partially separated soft and hard segments exist in the material. Hard segments can

form physical cross-links between themselves through hydrogen bonding and crystallization, making the material solid at below the melting or glass transition temperature of the hard segments. These hard segments are fixed for shape recovery. The soft segments can absorb most of the external stress applied on the polymers. The soft segments exist coiled in their unperturbed dimensions. At a temperature below T_g , micro-Brownian motion is almost negligible and the soft segment cannot gain enough kinetic energy to achieve the mobility. Thus, SMP are more difficult to deform in the glass state. Upon heating over T_g , however, micro-Brownian motion in soft segments is activated, and enough kinetic energy can be obtained to overcome the restriction for large-scale motion in the segments. Hence, above T_g SMP transit from the glassy state to the rubbery state can be easily deformed into its temporary shape. Thereby the soft and hard segments reorient themselves in the direction of external force, and the coiled soft segments are stretched causing an unfavorable chain conformation. By cooling SMPs below T_g while maintaining the load the micro-Brownian motion in soft segments is frozen. Thus, the elongated chains of the soft segments become fixed so that the deformation is maintained even after removal of the constraints. However, upon reheating above T_g micro-Brownian motion is triggered for action again. Soft segments achieve the mobility to return to its original coiled conformation. The hard segments from the physical cross links by way of polar interaction hydrogen bonding, with such cross-links being able to withstand moderately high temperature without being destroyed. This results in the recovery of the original shape of SMPs.

The structural demands to be fulfilled by shape memory can be realized by polyurethanes. The synthesis of polyurethanes usually involves diols and diisocyanates. For the synthesis of PUs used as SMP two different polydiols can be linked together by a diisocyanate resulting in the desired multiblock structure. The large number of available diols and diisocyanates allows adjusting the properties of polyurethanes in numerous ways according to a specific demand. E.g. the use of specific polyols allows adjusting the transition temperatures in such a way that the SME is triggered at a desired temperature sufficiently below the transition

temperature of the second polydiol, the transitions temperature which will determine the processing temperature.

The development and applications of PU with SME has created new demanding tasks for polymer analysis. The huge variety of available monomers allows the productions of PU with a large number of different structures and properties. In polyurethane based multiblock copolymers, the resulting PU can be heterogeneous in different ways. The most predominant heterogeneity is the one with respect to molar mass distribution (MMD). Since every polymerization implies statistical processes of chain initiation, growth, termination and transfer, chains of different lengths are formed, resulting in a molar mass distribution. Also, individual chains might vary in their comonomer composition giving rise to a chemical composition distribution (CCD). In addition functional end groups may be present, leading to a functionality type distribution (FTD). These heterogeneities in all cases might affect the final macroscopic properties of the material. Aiming to tailor the polymer properties for a particular application requires a fundamental understanding of the structure –property relationship of such materials. This in turn requires a detailed characterization of the complex products. This is also valid in the field of medical application where the rigorous and reliable proofs of a comprehensive characterization and quality control are needed. However, despite this increasing demand the methods for a detailed characterization of PU based multiblock copolymers remain rather limited.

Using spectroscopic methods without prior separation, one can only determine the type of monomer or functional groups present in the sample. However, these methods do not yield information on how different monomer units or functional groups are distributed among the polymer molecules. Finally, they in general do not provide molar mass information.

In order to adequately characterize multiblock (co)polymers it is necessary to determine not only average values of the chemical structure but a precise description of the multiple distributions is required in addition. Chromatographic separation techniques are particular valuable for this purpose. Size Exclusion Chromatography

(SEC) is the established method for analyzing polymer molar mass distribution as macromolecules are separated according to the hydrodynamic size in solution. Other suitable chromatographic techniques can be used to analyze the chemical composition distribution or the functionality type distribution of complex polymers. However, such separation techniques are often not readily available and need to be developed for a particular polymer system.

2. The Objectives of the Thesis

For the reasons stated above, the proposed project focuses on the development of new chromatographic characterization methods for the detailed qualitative and quantitative characterization of shape memory polymers. The polymers under investigation are polyurethanes composed of poly (ρ -dioxanone) (PPDO) and poly (ϵ -caprolactone) (PCL) segments.

The samples were produced by reacting mixtures of PCL- and PPDO-diols with a diisocyanate. This copolymerization process is expected to produce multiblock copolymers (MBC) with shape memory properties. However, the synthetic strategy might result in complex polymers, heterogeneous in both, molar mass and chemical composition. The distribution of the sample components might influence the SMP and thus needs to be characterized adequately. However, since no suitable methods existed, specific chromatographic techniques should be developed within this PhD thesis. The separation methods should allow for comprehensive characterization of complex polymer mixtures. As a first step a separation according to chemical composition was aimed for. Having established separation conditions the characterization of the fractions should be performed by applying different analytic techniques.

3. Theoretical Background

3.1 Molecular characterization of polymers

The simultaneous reaction of two different polyols and diisocyanate might result in multiblock copolymers formation. However, due to the statistical processes inherent in any polymerization process the products might be heterogeneous in both molar mass and chemical composition. It can be foreseen that only one analytical technique will not be sufficient to comprehensively characterize such complex products. Thus, combinations of several methods will be necessary [14]. The average values on chemical composition, end groups or molar masses can be obtained by spectroscopic and spectrometric methods. However, as spectroscopic and spectrometric methods will yield only average values but no information on the underlying distribution functions, the application of separation methods is required for a detailed characterization of the products. Separation techniques are useful to fractionate the samples by a certain characteristic feature and to obtain a distribution profile for this feature. On the other hand chromatographic methods as such separate but give no information on the structure of the separated species. It is beneficial to hyphenate separation methods with other spectroscopic or spectrometric methods. This allows obtaining qualitative and quantitative information e.g. on the chemical composition of the chromatographic fractions [15]. This results in highly detailed information on the chemical composition distribution of the sample. Also coupling two different chromatographic methods will allow resolving coeluting species, allowing determining e.g. correlations of chemical composition and molar mass of the macromolecular species.

3.1.1 Liquid Chromatographic Separation of Polymers

In order to separate polymers with respect to a specific structural feature, suitable chromatographic methods have to be developed. The method developments which have been conducted within this thesis were particularly focused on liquid chromatography. In the following section, a description of the principles of liquid

chromatography will be given with a special attention to the peculiarities of the technique when applied to polymer analysis.

3.1.2 Definition of liquid chromatography

Liquid chromatography is an analytical separation technique. The definition of the general term chromatography formulated by the International Union of Pure and Applied Chemistry (IUPAC) is as follows: "Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction" [16]. The IUPAC definition of the more specific term liquid chromatography is as follows: "A separation technique in which the mobile phase is a liquid. Liquid chromatography can either be carried out in a column or in a plane" [16]. Liquid chromatography can be divided, according to the mobile phase composition, in two groups of applications: isocratic analysis and gradient analysis. During isocratic elution, the eluent composition remains constant throughout the chromatographic experiment. In gradient elution, the eluent composition (and therefore eluent strength) is changed during the chromatographic run.

3.1.3 Separation modes in the chromatography of polymers

Chromatographic separations are processes where different analytes spend different times on their way through a chromatographic column. The different residence or retention times of different analytes are caused by the differences in the distribution equilibria of the solutes between the stationary phase and the mobile phase [31]. The well-known distribution coefficient K_d is the ratio of the concentrations of the analyte in the stationary phase to that in the mobile phase (i.e. $K_d = C_s/C_m$). It is related, thermodynamically, to the free energy difference, ΔG of the molecules in the two phases (mobile and stationary) [60]. The difference in free energy comprises enthalpic and entropic contributions [17]. The separation process in liquid chromatography can be described by:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_d \quad 3.1$$

$$\ln K_d = -\frac{\Delta G}{RT} = \frac{-\Delta H + T\Delta S}{RT} \quad 3.2$$

where, R is the gas constant, T the absolute temperature, ΔH and ΔS are the differences in enthalpy and entropy of the molecule in the stationary and the mobile phase, respectively.

When analyzing small molecules the enthalpic contributions are most of the time larger than the entropic contribution which is defined by the change in entropy due to the transfer of the analyte from the diluted mobile phase into the stationary phase where the analyte has a higher concentration. However, for macromolecules, the entropic contributions are more important as macromolecules are susceptible to adopt a large number of conformations. The conformation modification can be found in solution as the macromolecule enters the stationary phase pore (confinement of the macromolecules). The variation of entropy is a function of the volume of the polymer in solution and of the pore size distribution. Due to the large size of the macromolecules, they cannot penetrate the complete pore volume. Entering the pore from the free mobile phase causes a loss of entropy. Certain conformations of the polymer molecules simply do not fit into the pore [61].

Taking into account what has been mentioned above, this brief summary of possible thermodynamic contributions which are susceptible to occur when analyzing polymers, it is possible to define three kinds of chromatographic modes for polymer separation:

- Exclusion chromatography, where macromolecules are excluded from the pores of the packing material and thus are separated according to their size in solution (hydrodynamic volume): $0 < K_d < 1$. Thus, molecules with the largest volume in solution are eluted first and elution occurs in order of decreasing hydrodynamic volume. This mode of separation is only directed by entropic contributions.

- Adsorption chromatography, where chromatographic conditions are designed such that the polymer interacts with the stationary phase: $K_d \gg 1$. Since the molar mass increase with number of repeating units, macromolecules will be absorbed the stronger the higher its molar mass. Therefore the elution volume will increase with the molar mass of the macromolecules. This mode of separation is directed by enthalpic interactions.
- Critical condition chromatography, where enthalpic and entropic interactions compensate each other. Polymer chains are neither excluded from nor attracted by the stationary phase. Thus their elution volume is equal to the system hold-up volume: $K_d \approx 1$.

In addition to these three kinds of chromatographic modes, gradient chromatography is usually used for separation of polymers of very different adsorption strengths.

The use of each chromatographic mode depends on types of separation and information that has to be achieved. In the following more detailed characteristics of each chromatographic mode will be given.

3.1.3.1 Size exclusion chromatography

Molecular size or more precisely, hydrodynamic volume governs the separation process of sizes exclusion chromatography (SEC) [62-63]. That is as a mixture of solutes of different size passes through a column packed with porous particles, the molecules that are too large to penetrate the pores of the packing elute first because they have less access to the pore volume, and smaller molecules capable to penetrate or diffuse into the pores, elute at a later time or elution while volume. The large molecules that cannot penetrate the pores of the packing elute at the interstitial or void volume V_i of the column. The interstitial volume is the volume of the mobile phase that is located between the packing particles. As the molecular size of the molecules becomes smaller and begins to approach the average pore size of the packing, the molecules will penetrate or partition into the pores of the

packing at all and elute at a longer retention time. Finally, when the molecular size of the solute is small relative to the pore size, the molecules will freely diffuse into the pores sampling the total pore volume, V_p , of the packing. The elution volume of small solutes will be equal to the total mobile phase volume V_t of the packed SEC column

$$V_t = V_i + V_p \tag{3.3}$$

The dependence of retention volume on distribution coefficient in SEC can be described the general chromatographic equation

$$V_R = V_i + K_d V_p \tag{3.4}$$

where V_R is the retention volume or the elution volume of a solute and K_d is the SEC distribution coefficient.

In ideal SEC only exclusion from the pores of the packing material takes place, while no additional enthalpic contributions exist ($\Delta H = 0$). By considering the general thermodynamic equation 3.2, the distribution coefficient in ideal SEC can therefore be expressed as

$$K_d = K_{SEC} = \exp(\Delta S / R) \tag{3.5}$$

Due to the confined space of the pore the macromolecules cannot adopt all possible conformations. Therefore the conformational entropy ΔS decreases upon entering the pore from the free solution. Thus, ΔS takes negatives values and K_{SEC} has defined limits of $0 \leq K_{SEC} \leq 1$, i.e. the macromolecules elute before the total volume of the column.

In SEC the accessible volume for a macromolecule decreases with its increasing size, resulting in a decreasing elution volume with molar mass. After suitable calibration which is usually done by running several samples having narrow molar

mass distribution and known molar mass (for example polystyrene) , the molar mass distribution and the molar mass averages of a polymer sample can be determined.

3.1.3.2 Liquid adsorption chromatography

Liquid adsorption chromatography (LAC) is frequently utilized for separation of small molecules. In contrast to low molar mass analytes, polymers have a large number of adsorbable groups. These are all identical in the case of homopolymers but differ for copolymers. The number of the adsorbable groups increases with molar mass of a homopolymer. Therefore the total interaction energy and thus the distribution coefficient in adsorption chromatography increases also with the number of adsorbed monomer units. As a consequence, homopolymers elute at large elution volumes than the solvent band even if the interaction of a single repeating unit with stationary phase is weak. This behaviour can be described by the simultaneous adsorption of more than one repeating unit which is known as multisite attachment mechanism [18, 47,58-59]. The adsorption phenomenon implies a decrease of the enthalpic energy when adsorbing to the stationary phase. Thus, ΔH has a negative value and $K_{LAC} = \exp(-\Delta H/RT) > 1$. Therefore, if the interaction between the macromolecules and stationary phase is sufficiently strong, retention of the macromolecules will occur and the molecules will elute later than the solvent band. The polymer spends more time adsorbed on the stationary phase than the mobile phase.

The retention behaviour of a high molar mass polydisperse sample in LAC is different from a low molar mass monodisperse samples. Samples which consist of species differing substantially in molar mass or chemical composition cannot be separated isocratically because the different species would exhibit very different interaction strengths and therefore elution volumes. The higher molar mass polymers are strongly retained due to multiple attachments. The desorption of a strongly adsorbed macromolecules therefore requires displacement by a stronger eluent which in turn would reduce the retention of the lower molar masses. Therefore gradient methods are often applied, which will be described below. Since retention in LAC is strongly influenced by molar mass, minor differences in the

chemical structure as end groups or differences in topology might be hidden by the peak broadening due to the molar mass dependence. In order to achieve separations by end groups or other small structural differences one has to choose the conditions which allow a molar mass independent chromatographic elution.

3.1.3.3 Liquid chromatography at critical conditions (LC-CC)

As mentioned above in the size-exclusion mode the higher molar mass polymers are excluded from the pores and will therefore elute before the lower molar mass molecules. However, when the separation conditions favour adsorption, the retention order is inverted. The transition between these two chromatographic modes is observed under special conditions which are known as critical conditions. Under these conditions the molar mass dependence of retention time vanishes. The eluent composition at which this happens is called "critical composition". Chromatography performed under such conditions is referred to as chromatography at critical conditions of adsorption (LCCC) [17]. At critical conditions the entropic losses due to the exclusion of the molecules from the pores of the stationary phase are exactly compensated by the enthalpic gains due to interaction of molecules with the stationary phase hence $T\Delta S = \Delta H$ [64-65]. Accordingly, $\Delta G = 0$ and the distribution coefficient is $K_d = 1$, irrespective of the molar mass of the polymer molecules [66-72]. Under these conditions, which are sensitive to small changes of temperature or mobile phase composition, macromolecules of a given chemical structure elute at the same elution volume, irrespective of their molar mass, as depicted in Fig. 3.1 [73]. The critical conditions are experimentally determined by examining the molar mass dependence of retention times of the respective homopolymer at different isocratic eluent compositions. The critical conditions are identified as the eluent composition at which the retention of homopolymer becomes independent of its molar mass. Since at critical conditions the elution volume of an end-functionalized homopolymer is not affected by the molar mass of the polymer chain, LCCC can be used to separate homopolymers having different end groups provides these end groups differ in their adsorption strengths. Consequently, a functional type distribution (FTD) of polymers can be obtained [19-20,74-82]. Also block copolymers or graft copolymer can be

characterized by LCCC [21-23, 48-49,83-90]. If critical conditions are realized for the polymer forming one block, this block will not contribute to the retention of the block copolymer any longer. Therefore the retention will be determined by the other block only. The homopolymer forming that block might thereby elute either in SEC or in LAC elution order [83]. If a calibration is made with the respective homopolymer, the molar mass distribution of a single block in a block copolymer can be determined. A review has been written detailing the principles of the technique and summarizing critical conditions for a large variety of polymers [24]. The determination of the critical conditions of elution for a polymer is frequently a time consuming experimental process. Indeed critical conditions are very sensitive and slight deviations of the mobile phase from the critical composition can change the retention mode to SEC or LAC.

3.1.3.4 Gradient liquid chromatography

Since isocratic elution at adsorbing conditions has its difficulties when polymers of very different adsorption strengths need to be separated, gradient chromatography is used frequently in polymer chromatography. In gradient chromatography the eluent strength is varied systematically during the chromatographic experiment. This is usually done by changing the eluent composition. The mechanism of gradient elution in polymer chromatography remains still more difficult to understand as compared to that of isocratic chromatography. From a thermodynamic point of view, both enthalpic and entropic effects are operative in polymer gradient elution. However, like in LAC, the enthalpic effects are more dominant ($T\Delta S \ll \Delta H$). At the start of gradient, the polymer molecules are adsorbed strongly in the weak initial eluent composition, i.e. $K_d \gg 1$. Polymer molecules of high molar mass are more strongly adsorbed than those of lower molar mass. By increasing the eluent strength desorption occurs (K_d decreases) with weakly adsorbed molecules desorbing first. Therefore, lower molar mass molecules elute earlier than those of higher molar masses. At sufficiently high molar masses, a nearly molar mass independent elution is observed. Retention processes have been discussed by Snyder and others and tests have been suggested to identify the actual operative mechanism [32-33].

The macromolecules start eluting when the composition of the mobile phase becomes close to their critical conditions: $\Delta G \approx 0$. This corresponds to the point where adsorptive interactions are dramatically reduced by the proportion of eluting solvent in the mobile phase and they reach the same order of magnitude than entropic contributions. As these desorbing conditions differ according to the chemical composition of the chains (the nature of the repeat unit is responsible for the interaction strength), a chemical composition distribution is determined: similar fractions of macromolecules will elute from the column together independent of the molar mass with a mobile phase composition close to their critical conditions [34,27,42,43]. Since the critical composition strongly depends on the chemical nature of the polymer molecule a separation according to chemical composition can be achieved. Therefore gradient chromatography is often applied for separation of polymers blends or copolymers according to chemical composition [36-41].

The kinetics of the dissolution of the polymer in the eluent may then further complicate the mechanism of gradient elution. At this stage, it is generally accepted that the mechanisms of gradient elution of high molar mass polymers will depend on the sample, the concentration of sample injected onto the column, on the choice of mobile phase and on the strength of the interaction between the sample and the stationary phase.

Usually the three modes of chromatography are represented on the same diagram showing the effect of the molar mass on the elution volume. Gradient liquid chromatography can also be figured on this plot as showed in Fig. 3.1.

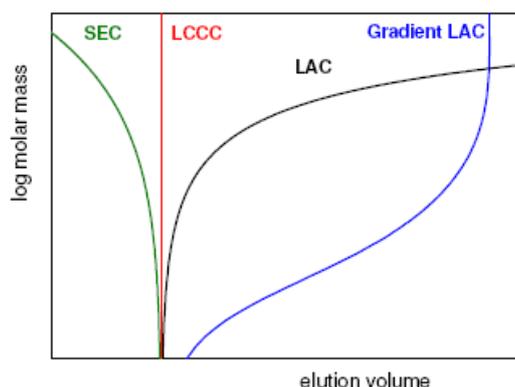


Figure: 3.1: Schematic representations of the molar mass dependences of elution volume in polymer liquid chromatography [45].

3.2 Detection and identification of polymers

The preceding sections have given an overview on the separations that can be obtained in the different modes of polymer chromatography. After the separation step the macromolecules must be identified. For this, there are different types of instruments that can be used depending on what kind of information needs to be achieved. In this thesis, Evaporative Light Scattering Detector (ELSD), LC-FTIR, LC-NMR and pyrolysis GC-MS were used. An overview of methods and instruments used will be given next.

3.2.1 Evaporative Light Scattering Detector (ELSD)

One type of detector widely used in chromatography of polymers is the Evaporative Light Scattering Detector (ELSD). The evaporative light detection system has the advantage to be useful even under gradient conditions. The ELSD process involves three steps: nebulization, evaporation and detection.

In the first step which is nebulization, the eluent stream enters the detector at the bottom of the evaporation chamber. It passes through a heated nebulizer. A continuous flowing nitrogen gas shears droplets which then pass as a continuous stream into the evaporator. The size and uniformity of the droplets are extremely important in achieving sensitivity and reproducibility. The applied ELSD uses a concentric gas nebulizer and a constant flow of an inert gas to achieve the required

consistency. After the nebulization, the next step is the evaporation during which the spray moves through the heated evaporation tube assisted by the carrier gas. In the evaporation tube the solvent is volatilized to produce particles or droplets of the pure non-volatile analyte. The tube provides evaporation of solvents at low temperatures to minimize evaporation of the analyte. The last step refers to the detection. The particles emerging from the evaporation tube enter the optical cell, where the analyte particles pass through a beam of light where the light is scattered at the particle. The amount of light detected is proportional to the solute concentration and solute particle size distribution.

The ELSD is relatively easy to set up and can be used even in gradient chromatography. However the response depends on a variety of parameters which influence the formation of the particles. Analyte concentration in the mobile phase when it reaches the detector is definitely the most important factor for ELSD [46]. But it has to be taken into account that a high sample concentration is susceptible to favor formation of larger particles hence giving a more intensive response. Other influencing factors are the mobile phase composition and flow rate which both change the quality of the evaporation. As the detection process might be affected by the size of the droplets of the liquid, the rate of evaporation and the nebulizer gas flow, then it is important to maintain steady conditions both internal and external to during the all experimental.

3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy is an excellent tool for characterizing polymers. It yields information on the overall chemical composition and the presence or absence of specific functional groups in the polymer molecules. FTIR has the advantages of speed and sensitivity. It can be applied as an on-line technique after separation by LC with a specific flow-cell. However, solvent adsorption remains the main limitation when using a flow cell. This is because the major parts of the spectrum might be completely obscured by solvent absorbances. This drawback can be overcome by using a special interface, (LC-Transform) to remove the solvent before acquiring the FTIR-spectra of the fractions. Therefore this setup requires two

steps: first deposition and then analysis of the spectra. The most important element of the interface is a heated nozzle positioned above a moving Ge-plate. The eluent is heated upon flowing through the nozzle. At the same time the back pressure of the nozzle decreases towards the end of the nozzle resulting in solvent evaporation at the nozzle end. Non-volatile substrates will not evaporate but deposit on the Ge-plate. Due to the Ge-plate motion, sample fractions corresponding to different chromatographic elution times will be deposited at different positions on the Ge-plate. For polymers, which usually are not separated into separated peaks, usually a film like deposition is observed. After ending the chromatographic experiment the Ge-plate is transferred and placed in a special optical device within the FTIR spectrometer for the analysis of deposited fractions. FTIR spectra are taken at regular intervals along the polymer film. The lower surface of the Ge-plate is coated with aluminum, rendering it reflective. Therefore infrared energy is directed from the FTIR source onto the sample deposit. The FTIR beam passes through the deposit and the Germanium to the reflective surface. The laser beam is reflected from this surface back through the sample, and then to the FTIR detector. The result is a dual-pass transmission measurement of the sample. Afterwards, the spectra are analyzed by means of specific software and then interpreted in order to identify the structure of the compounds of interest. Albrecht et al. used this technique to determine the chemical composition distribution of copolymer species [15].

3.2.3 Nuclear Magnetic Resonance (NMR)

Another useful technique for quantification of polymers is NMR. It is one of the most informative methods for structural characterization of polymers. NMR provides much more and detailed information on the polymer. Similar to FTIR, NMR as a stand alone technique provides only average information on the sample. In order to study complex polymers hyphenation of liquid chromatography and NMR is a useful approach. Hyphenation of liquid chromatography and NMR can be done off- or on-line. When carrying out off-line experiments, contamination and decomposition of the sample might happen and might affect the final results. Therefore, the application of on-line LC-NMR is superior. However, two problems exist in coupling

NMR to chromatography. On-line LC-NMR experiments require the use of solvent suppression techniques because the solvent suppression allows recording a weak signal of the solute in the background of dominating solvent peak. This technique is well suited for isocratic LC separations (e.g. SEC separations) but remains difficult to implement for gradient chromatography. The major problem with on-line NMR is the lack of sensitivity of NMR spectrometry in conjunction with the low sample concentration used in liquid chromatography, which limits the use of this coupling technique. This is the major reason why on-line proton LC-NMR is generally the tool of choice as compared to ^{13}C -NMR. Compared to off-line LC-NMR, on-line LC-NMR will probably give accurate information on the chemical composition and structure elucidation because it permits the direct analysis of the chemical composition at each elution volume of the chromatogram. Hiller et al. showed by coupling a LCCC separation with ^1H -NMR that it is possible to determine in one experiment the molar mass distribution and chemical composition of the copolymers [26].

3.2.4 Pyrolysis GC-MS

Pyrolysis GC-MS has been used extensively as an analytical technique in which large molecules are degraded into smaller volatile species using only thermal energy. Pyrolysis, combined with modern analytical methods, such as gas chromatography and mass spectrometry (Py-GC-MS) is a very useful technique for analysis of polymeric materials.

Py-GC-MS needs less than 100 μg of the original material to be analysed directly. Pyrolysis involves a thermal dissociation of materials in an inert atmosphere (in presence of He). Large molecules cleave at their weakest points and produce smaller, more volatile fragments. A flow of inert gas (He) flushes the pyrolysates into the GC-column, where the different analytes will be separated. The stream of separated compounds is fed on-line into a mass spectrometer. The mass spectrometer uses an ion source, containing a metallic filament to which high voltage is applied. This filament emits electrons which ionize the compounds. The ions are

further fragmented, yielding predictable patterns of the component. Intact ions and fragments pass into the mass spectrometer's analyzer and are eventually detected.

4. Results and Discussions

In this part, results of the chromatographic method development for the functionality type distribution (FTD) of PPDO- and PCL-diols and multiblockcopolymers (MBC) separation is reported. FTD of PPDO- and PCL-diols was performed in order to determine the end groups. The analyses of the MBCs were mainly conducted in order to obtain structural and compositional information on products with the aim of understanding the copolymerization and by this mean optimizing the reaction synthesis. The results are divided in two main parts. The first is dedicated to the study of the FTD of PPDO and PCL-diols. In the second part the MBCs are analyzed. The macrodiols used for the synthesis of the multiblock polymers (MBP) are p-dioxanone (PPDO) and ϵ -caprolactone (PCL) diols. PCL-diols are commercially available, while PPDO-diols are not. Thus, the PPDO-diols were synthesized by ring opening polymerization from commercially available p-dioxan-2-one (PDO) with a diol as initiator. The multiblock polymers (MBP) of PPDO and PCL were synthesized by reacting the respective macrodiols (PPDO or PCL-diols) with trimethyl hexamethylene diisocyanate (TMDI) in solution at elevated temperature. The MBCs used in this study were synthesized as one-step reaction by simultaneously mixing the macrodiols (PPDO- and PCL-diols), and TMDI, together in the solvent and heating the solution at elevated temperature. The schematic synthesis of PPDO-diols, MBP and MBC is reported in experimental part.

The molecular parameters of different ϵ -caprolactone (PCL)diols, p-dioxanone (PPDO)-diols, mutiblock polymers (MBP) and multiblock copolymers (MBC) samples given by the supplier are listed in Table 4.1.

Table 4.1: Molecular parameters of different PCL and PPDO diols, MBPs and MBCs samples as given by supplier.

Sample ID	Abbreviation	M_n ($\text{g}\cdot\text{mol}^{-1}$)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	Composition wt% (PPDO/PCL)
poly (ϵ -caprolactone)	PCL-2205	1800	2600	0/100
poly (ϵ -caprolactone)	PCL-2304	3000	3900	0/100
poly (ϵ -caprolactone)	PCL-2403	4200	5700	0/100
poly (ϵ -caprolactone)	PCL-2803	8400	113000	0/100
poly (p-dioxanone)	PPDO-5.8	4600	9400	100/0
poly (p-dioxanone)	PPDO-12	3200	4700	100/0
poly (p-dioxanone)	PPDO-10	4100	6200	100/0
PCL-MBP	LP 065	19000	74000	100/0
PPDO-MBP	LP 056	59000	159000	0/100
PPDO-10/PCL2k	LP099	54000	160000	50/50
PPDO-10/PCL2k	LP 027	60000	181000	50/50
PPDO-5.8/PCL10k	LP101	32000	13.0000	50/50
PPDO-12/PCL2k	LP102	29000	111000	50/50
PPDO-12/PCL2k	LP103	29000	115000	50/50
PPDO-14/PCL2k	LP126	38000	70000	60/40
PPDO-14/PCL2k	LP127	29500	95000	60/40
PPDO-12/PCL2K	LP 166	25000	259000	50/50

Please note that different numbers after PPDO represents the batch# for the polymerization of PPDO from commercially available PDO. PCL is caprolactone purchased from solvay chemicals (2k and 10k represent the molar mass). M_n being the number average molar mass and M_w being the weight average molar mass

4.1 Functionality Type Distribution (FTD) of PCLs and PPDOs-diols

As mentioned above, the first section of the results deals with the functionality type distribution (FTD) of functionalized PCL and PPDO-diols in order to check the purity of the samples. Since these diols were used for the synthesis of the MBCs, the functionality analysis will allow gaining information on the end group of the resulting final MBC.

4.1.1 Separation of PCL-diols according to functional hydroxyl groups

The task here was to separate PCL-diols samples according to end groups. PCL-diols were purchased from solvay chemicals while PCL-monool was obtained in house (DKI). The monool is needed to check for the molar mass independent elution with other PCL-diols samples. Since it is not easy to determine the liquid chromatography at critical conditions (LCCC) by using functionalize PCL-monool and PCL-diols, because they cannot elute at the same retention time. For this reason, first the PCL-monool and PCL-diols were modified in such a way that the resulting end group should not interact with the stationary phase and decrease the retention. In this case, for the modification of the hydroxyl function, acetyl chloride was selected aiming to form the terminal acetate groups. The modification reaction is illustrated in Fig. 4.1.

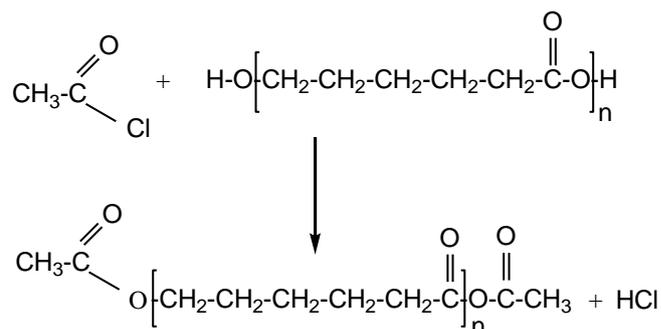


Figure 4.1: End capping of PCL-diols by acetyl chloride

Aiming to perform the separation of polar end groups, a normal phase column (Nucleosil-NP, particle size 7 μm , pore diameter 1000 \AA , column dimension 250mm \times 4.0 mm) was used. Beside the stationary phase a suitable mobile phase had to be selected. It was necessary to find two suitable solvents which will form the mobile phase. One solvent should cause complete adsorption of PCL, while the other solvent should result in complete desorption from the stationary phase. By isocratic experiments it was established that DCM acts as adsorption promoting solvent, while the application of THF to DCM results in desorption. In order to perform LCCC for the PCL-samples it was required to determine the critical conditions for PCL. The gradient chromatography experimental was performed. As discussed in section 3.1.3.4 the composition at which a high molar mass homopolymer elutes within a gradient is expected to be close to the critical eluent composition. Thus, based on the elution volume of high molar mass PCL-diols in the linear gradient and using equation 4.1 [27], the critical eluent composition was estimated to be close to 74%/26% (v/v) of DCM/THF.

$$\%B_g = (V_g - V_v - V_d) \frac{\Delta \%B_g}{F t_G} + \%B_0 \quad 4.1$$

Here V_g is the elution volume in the gradient, V_v is column void volume, V_d the system dwell volume. $\Delta \%B_g$ is the change in eluent composition (of strong eluent) during the gradient, t_G the gradient time, while F is the flow rate and $\%B_0$ the initial eluent composition. From this composition (74%/26% of DCM/THF), isocratic experiments were performed by systematically varying the mobile phase composition until a molar

mass-independent elution was observed, which characterizes critical elution behavior. Molar mass independent elution was observed at a solvent composition of 92/8 (DCM/THF v,v). Fig.4.2 shows the chromatograms at critical conditions of modified end group for PCL-monool and PCL-diols of different molar masses.

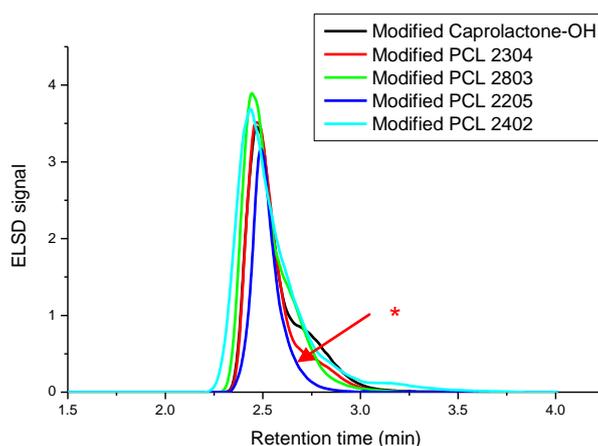


Figure 4.2: Chromatograms at LCCC for modified PCLs end group for PCL-monool (black) and PCL-diols. Sky blue M=4kg/mol, Dark blue M=2kg/mol, Green M=8kg/mol, Red M=3kg/mol. (Column: Nucleosil-NP, (250 × 4.0 mm), 7 μ m, 1000 Å , Flow Rate: 1 mL / min, Injection Volume: 100 μ L, Detector: ELSD, Critical composition: 92%8% (DCM-THF v/v), Temperature: 35°C).

One can see that all samples exhibit the same retention time irrespective of their molar mass. This indicates that the eluent composition of 92%8% (DCM-THF v/v) coincides with the critical eluent composition.

For two of the samples a shoulder at 2.95 min (marked by * in Fig. 4.2) is observed. This shoulder might be due to an incomplete end capping reaction of the OH-groups by the acetyl chloride. The non end-capped molecules are expected to interact with the stationary phase. This might be the reason why the experimental critical conditions are so far from the expected composition.

4.1.1.1 Analysis of PCL-monool and PCL-diols at critical conditions

After determining the LCCC the PCL-monool and PCL-diols were examined under the same chromatographic conditions. Fig. 4.3 shows the chromatograms of the PCL-monool and the PCL-diols at an eluent composition of 92%8% (DCM-THF v/v).

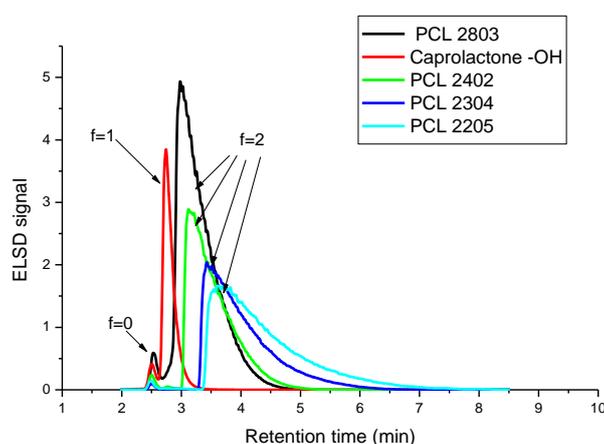


Figure 4.3: Chromatograms of PCL-monool and PCL-diols at critical conditions for PCL. PCL-monool (red) and PCL-diols. Sky blue $M=2\text{kg/mol}$, Dark blue $M=3\text{kg/mol}$, Green $M=4\text{kg/mol}$, Black $M=3\text{kg/mol}$. (Column: nucleosil-NP, (250 × 4.0 mm), 7 μm , 1000 Å , Flow Rate: 1 mL / min, Injection Volume: 100 μL , Detector: ELSD, Critical composition: 92%8% (DCM-THF v/v), Temperature: 35°C.

In Fig. 4.3 one can see that all samples exhibit different retention times due to the interaction of the OH-groups with stationary phase.

All polymers show a small peak at 2.5 min. This peak corresponds to the elution volume of the modified PCL. Here it acts thus around PCL molecules, which do not exhibit OH-groups. Immediately after this peak elutes the PCL-monool at 2.7 min. This is due to the additional adsorption effect of the OH-group. Consequently the diols elute at higher retention times, due to the additional retention caused by the second OH-group. In addition it can be observed that the PCL-diols elute in order of decreasing molar mass. Since under critical conditions the adsorption of the repeating units should not contribute to the retention, the reason of this elution behaviour might be due to the fact that with increasing molar mass the two OH-end groups are only adsorbed statistically independently. If the polymer chain is however

short, then the two end group adsorb no longer independently. If the first OH-group is adsorbed, then also the second OH-group is in the proximity of the stationary phase and the probability for its simultaneous adsorption is increased [44]. In this way, the effect should be stronger for short polymer chains than for longer polymer ones. In other words: the longer the polymer chain is, the less will the adsorption of the first functional group influence the adsorption of the other one. As a consequence, polymers with increasing molar mass elute before those of lower molar mass as can be observed in Fig. 4.3.

4.1.1.2 Separation of PPDO-diols according to end group functionality

The separation of PPDO-diols according to end group functionality was planned to be performed similar to the PCL-diols. However, a number of difficulties were encountered with PPDO-diols. However, firstly, the PPDO-diols available were unknown in terms of purity if the OH were the end groups. Secondly, two of available PPDO-diols had almost similar molar mass. Therefore, it was not possible to determine critical conditions in the common way by proving molar mass independent elution for a series of samples of different molar masses.

In order to overcome the problems mentioned above, the separations of PPDO-diols were finally performed using gradient chromatography. Aimed at the separation of polar end-groups, a normal phase (Nucleosil (bare silica), particle size 7 μ m, pore diameter 1000 Å, column dimension 250 mm \times 4.0 mm) column was selected. Based on this selection of stationary phase two suitable solvents had to be identified, one of which should cause complete adsorption of PPDO-diols on the stationary phase, while the other should completely desorb PPDO-diols. DCM and dimethylformamide (DMF) were found to fulfill these criteria. The linear gradient ranging within 10 minutes from 100% DCM to 100% DMF was used. 100% DMF was hold for 1 minute before returning to the initial composition. Finally, a re-equilibration of the column was allowed for 5 min with DCM.

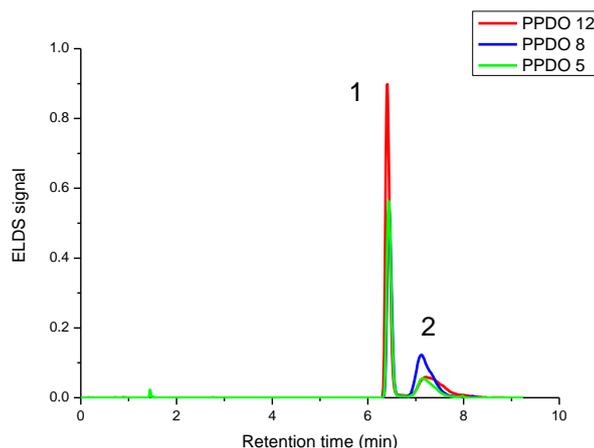


Figure 4.4: chromatograms of the PPDOs: Red M= 4,7kg/mol, Green M= 9,4kg/mol, and Blue M= 8,2kg/mol mobile phase DCM-DMF, Column: Macherey&Nagel Nucleosil (250 × 4.0 mm, 7 μ m, 1000Å) Flow Rate: 1 mL / min, Injection Volume 50 μ L, Detector: ELSD, Critical Temperature: 35°C.

Under these chromatographic conditions, the different PPDO-diols eluted in two separated peaks as shown in Fig. 4.4. This indicates that the samples are not homogeneous but contain species of different structures. In order to increase resolution which would ease fractionation, the chromatographic conditions were modified. The modified gradient runs from 100% DCM to 40% DMF within 10 min. The 40% represents the lowest DCM content where all samples elute from the column.

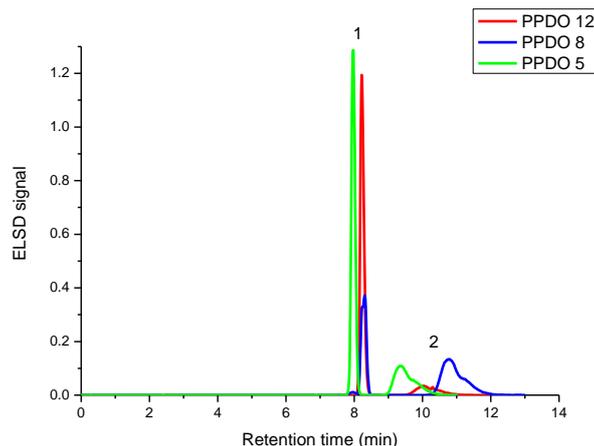
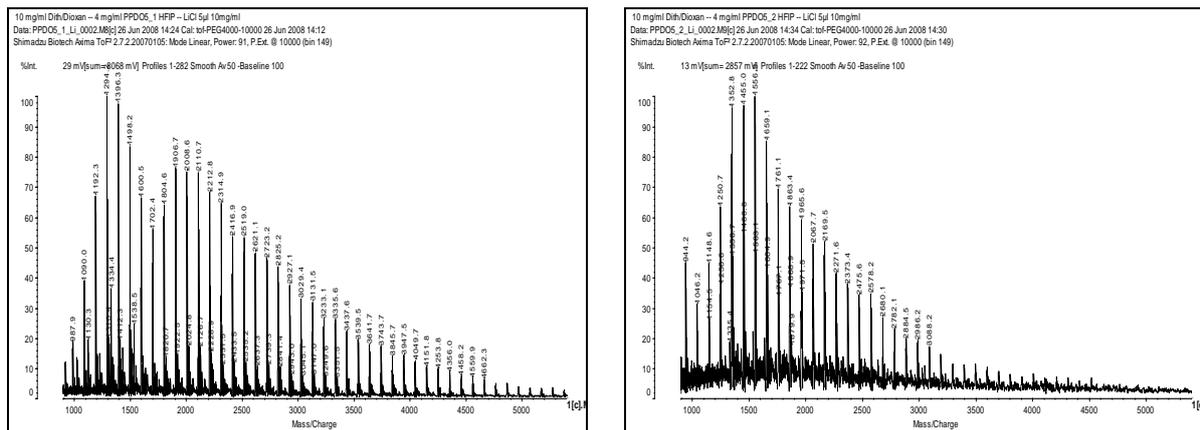


Figure 4.5: chromatograms of PPDOs: Red M=4,7kg/mol, Green M= 9,4kg/mol and Blue M=8,2kg/mol, mobile phase DCM-DMF (60/40 v,v), Column: Macherey&Nagel Nucleosil, (250 × 4.0 mm, 7 μ m, 1000Å) Flow Rate: 1 mL / min, Injection Volume 50 μ L, Detector: ELSD, Critical Temperature: 35°C.

Fig. 4.5 shows the chromatograms of PPDOs-12, 8 and 5 (Red M=4,7kg/mol, Green M= 9,4kg/mol and Blue M= 8,2kg/mol) obtained using the modified gradient. The new gradient indeed results in a better separation of the two peaks. In order to obtain information on the structure of the polymers eluting in the two peaks the samples were manually fractionated several times. Afterwards the solvent was evaporated and the polymer was analyzed by MALDI-TOF-MS.



differences in the initiator or the end groups. In the present case, based on the manufacturer's information the PPDOs have been initiated by different low molar mass diols, e.g. ethyleneglycol, which related to a series of peaks expected which can be described as:

$$m/e = (p+q) \times 102.02 + 62 + 7$$

where m/e = experimentally determined peak mass, $(p+q)$ degree of polymerization, 7 (mass of counterion $\text{Li}^+ = 7 \text{ g/mol}$) and m = mass of initiator (i.e. $m=62 \text{ g/mol}$). By using this formula the following structure should result:

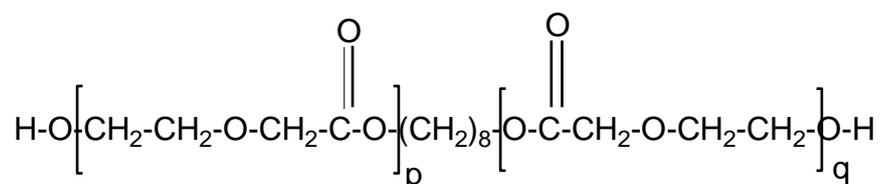


Figure 4.8: Schematic representation of an ethylene glycol of starting PPDO-diol

Based on the formula given above the following expected masses for the MALDI-TOF-spectrum can be calculated which correspond to the series in fraction 1 (▼).

	p+q	m/e (expt.)	m/e (th.)
▼	13	1396.3	1397.4
▼	14	1498.2	1499.4
▼	15	1600.5	1601.5
▼	16	1702.4	1703.5

For the main series (▲) in fraction 2, the experimental masses are close to the masses calculated using the following formula: $m/e = (p+q) \times 102.03 + 18 + 7$. This formula would be valid if one assumes that it corresponds to a PPDO, which has on one side a carboxyl function and an OH-group on the other side as illustrated in Fig. 4.9. These chains might originate from small amounts of water present during the polymerization. The water results in a saponification of PDO to the corresponding PPDO which in turn initiates a polymerization of chain. The corresponding

structures are linear PPDOs having a hydroxyl- and a carboxyl functionality. A comparison of the calculated and experimentally observed masses is given below.

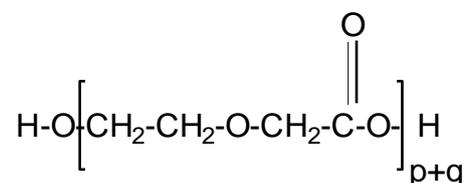


Figure 4.9: PPDO with carboxyl-and OH-end group.

	p+q	m/e (expt.)	m/e (th.)
▲	14	1453.4	1455.0
▲	15	1555.5	1556.9
▲	16	1657.5	1659.1
▲	17	1759.5	1761.1

The signals of the second series of fraction 2 are marked (●) in Fig. 4.7 shows the shifted further 6 mass unit, it acts then around the same molar mass and structure with series (▲), but here the hydrogen atom is replaced by Li.

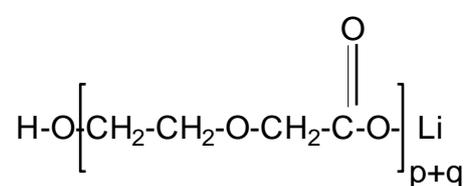


Figure 4.10: PPDO with OH- and Li-Carboxylate

In a third series (X) of fraction 2 the experimental masses are close to the masses calculated using the following formula: $m/e = (p+q) \times 102.03 + 7$. This formula is in agreement with cyclic structures which might be formed by intramolecular cyclisation reaction between hydroxyl- and carboxylic end groups.

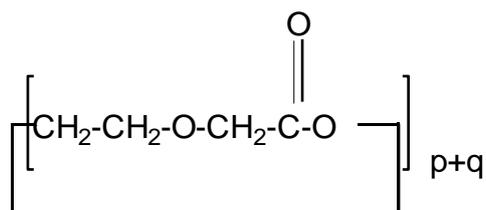


Figure 4.11: cyclic PPDO

	p+q	m/e (expt.)	m/e (th.)
X	14	1436.4	1435.2
X	15	1538.5	1537.5
X	16	1640.4	1639.5
X	17	1743,1	1741.5

The results of the MALDI-ToF experiments on the chromatographic fraction clearly show that the target compounds, carrying two hydroxyl functions, elute within the first peak. The second peaks for the different samples are composed of PPDOs carrying one hydroxyl- and one carboxyl functionality (or its Li-salt). These chains might result from an undesired side reaction with water. Since the higher polar chains are expected to have a larger retention time than less polar ones, the assigned structures are in disagreement with the observed elution order. Beside the mentioned structure some cyclic by-products were identified as well. The results obtained above are also verified for PPDOs 8 and 12. Octandiol has been used as initiator for the PPDO-12 synthesis based on the information given by manufacturer.

4.2 Characterization of chemical heterogeneity of multiblock copolymer (MBC)

In this part of the study, results of the chromatographic method development for multiblock copolymer (MBC) samples which have been synthesized by GKSS Forschungszentrum Geesthacht GmbH will be presented. These MBCs were prepared in order to improve the properties and potential of the resulting shape memory polymers for medical application. The final goal of the analysis of the MBCs was to gain information on the extent of chemical heterogeneity of the products. This

information would help to understand how the heterogeneity of the product influences the properties of the final products and how the extend of heterogeneity is affected by the synthesis methods.

The MBCs under investigation were all synthesized by reacting simultaneously poly(ρ -dioxanone)-(PPDO) and poly(ϵ -caprolactone) (PCL)-diols with trimethyl hexamethylene diisocyanate (TMDI). Since the coupling reaction should result in the formation of urethane linkages, the materials are called polyurethane multiblock copolymers.

As every polymer synthesis involves statistical processes, the MBCs were expected to present heterogeneities in both molar mass and chemical composition. In order to get first information on the heterogeneity with respect to molar mass size exclusion chromatography (SEC) was performed. In addition SEC-FITR experiments were performed to determine potential compositional changes across the molar mass distribution (MMD) and thus to obtain first information on chemical heterogeneity.

4.2.1 Analysis of molar mass distribution by SEC

The MBCs were at first analyzed by SEC in order to determine M_n and M_w . A typical example of a SEC separation of a MBC is shown in Fig. 4.12 for MBC LP 102.

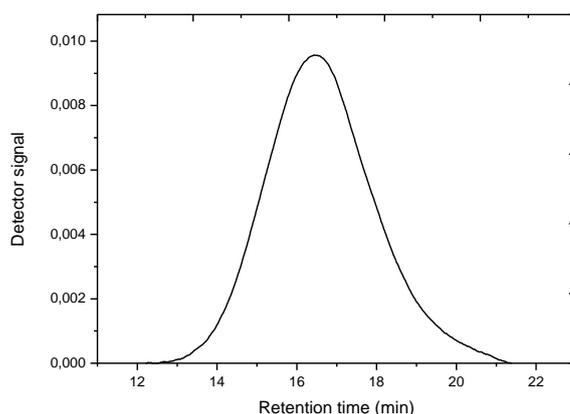


Figure 4.12: SEC chromatogram of MBC LP 102, stationary phase: PSS SDV 10^3 , 10^5 Å (each 300 x 8 mm I.D.), mobile phase: CHCl_3 , flow rate: 1 mL/min, detection: RI

A monomodal elution profile is observed which was converted into a monomodal MMD upon applying a polystyrene calibration curve. The SEC analysis for the other MBCs also provided monomodal MMD. For each MBC, both average molar masses were determined: M_n and M_w . The M_n values for the MBCs were found to be between $M_n=1800$ - 9800 g/mol and $M_w=17000$ -33000 g/mol. The PDIs varied between 3.3 and 5.8. The molar mass and PDIs results of the MBCs are reported in Table 4.2.

Table 4.2: Average molar masses and PDIs of the MBCs obtained versus PSS standards

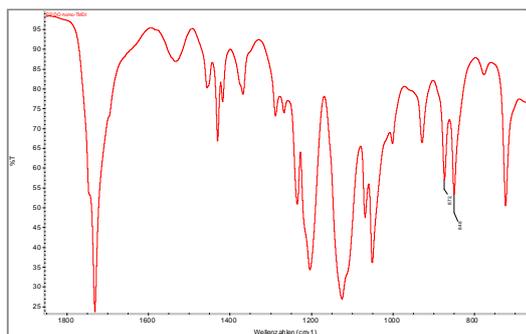
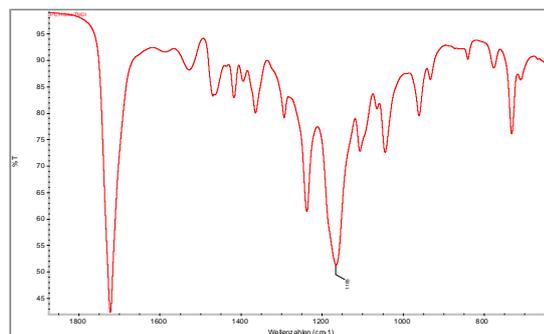
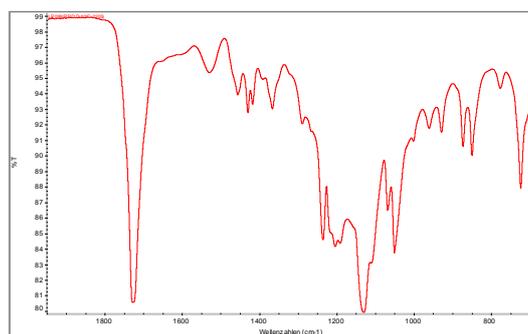
Samples	M_w (g \times mol $^{-1}$)	M_n (g \times mol $^{-1}$)	PDI
LP 099	33 000	9 800	3,3
LP 101	32 000	9 200	3,4
LP 102	28 000	6 600	4,1
LP 103	27 000	5 000	5,4
LP 126	30 000	6 600	4,6
LP 127	18 000	3 800	4,7
LP 166	17 000	2 900	5,8

In Table 4.2 one can see that the molar mass obtained are in contrast to those given by producers in Table 4.1. The differences of these molar mass might come from the calibration curve. Because using different calibration curves for molar mass determination, it is obvious that a huge error can result on the final values. Therefore, for the comparison of the results of different laboratories, it is absolutely necessary to use the same experimental conditions in particular the calibration standards and the eluent.

4.2.2 Investigation of chemical composition by SEC- FTIR

SEC alone cannot provide any information about the chemical composition of the MBC. In order to obtain first information on possible chemical heterogeneity of the MBC, SEC-FTIR appears to be the method of choice at this early stage of the research.

However, before applying SEC-FTIR, it is necessary to find out about differences in the FTIR-spectra between PPDO and PCL- diols. Therefore, FTIR spectra of PPDO-diols, PCL-diols and a MBC (LP 101) were recorded as illustrated in Figs. 4.13, 4.14 and 4.15

**Figure 4.13: FTIR spectrum of PPDO-diols****Figure 4.14: FTIR spectrum of PCL-diols****Figure 4.15: FTIR spectrum of MBC LP 101**

At the first glance the FTIR spectrum of PPDO-diols in Fig. 4.13 and FTIR spectrum of PCL-diols in Fig. 4.14 show the same group vibration characteristic at 1700cm^{-1} characteristic of carboxylic group. By examining closely these two spectra, it appears that the PPDO- spectrum shows two bands at $848\text{-}874\text{ cm}^{-1}$ which do not show up in the PCL-spectrum. The PCL-spectrum, however, shows an intense band at 1167 cm^{-1} which is absent in the PPDO-spectrum. These two bands might therefore be useful to identify each component.

The FTIR-spectrum of MBC LP 101 in Fig. 4.15 shows the presence of the bands characteristic for both PPDO- and PCL- diols. This indicates that PPDO and PCL are present in the MBC.

Having identified characteristic bands for PPDO and PCL, it was possible to use SEC-FTIR to determine a peak ratio which is related to compositional changes across the molar mass distribution of the MBCs. This operation was done by measuring the peak heights (I_1) at 1146cm^{-1} (CHOH) and the peak height (I_2) at 1178cm^{-1} (COH) slice by slice. The ratio was determined by dividing I_1/I_2 . Figure 4.16 illustrates the variation of the peak ratio across the chromatograms in different MBCs.

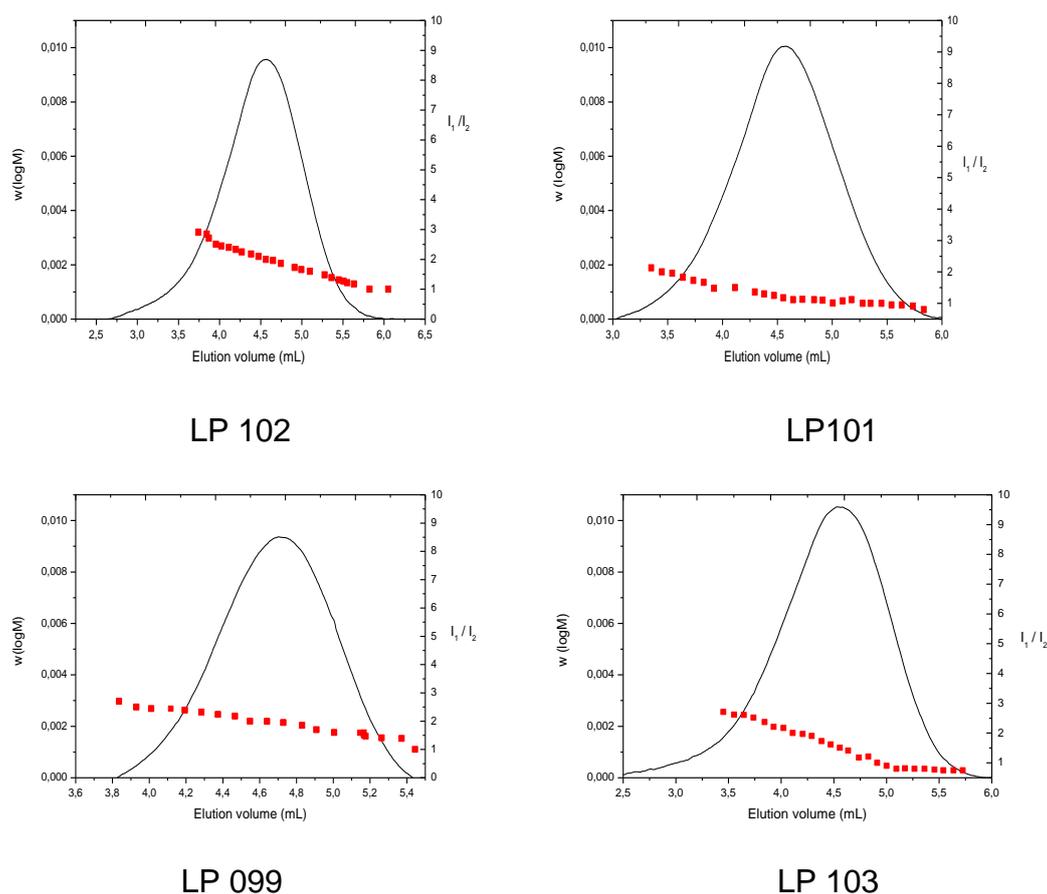


Figure 4.16: Chromatogram (black curve) and peak ratio (red squares) from SEC-FTIR of the MBCs LP 102, 099, 101 and 103 stationary phase: PSS SDV 10^3 , 10^5 Å (each 300 x 8 mm I.D.), mobile phase: CHCl_3 , flow rate: 1 mL/min, detection: RI

Fig. 4.16 shows the chromatogram (black curve) together with the variation in relative FTIR peak intensities, which correspond to the variation in the chemical composition (red squares) for different MBCs. Since I_1/I_2 is proportional to the PPDO content, the decrease in I_1/I_2 with increasing elution volume indicates a decrease in PPDO content as molar mass decreases. Obviously, this indicates that the MBCs samples contain species of very different molar masses. The SEC-FTIR results clearly revealed differences in chemical composition of the samples. However, from the given data, it is not possible to answer the question whether the two chemical structures (PPDO and PCL) are combined to yield a copolymer with varying composition or whether blends of the two MBPs (PPDO-MBP and PCL-MBP), having different MMD (or to be more precise different hydrodynamic volume distributions),

exist. The reason is that SEC separates by molecular size and not by chemical composition. Thus, in order to get more precise information on chemical composition distribution (CCD) a separation according the chemical composition was required. Such separations can be achieved by gradient high performance liquid chromatography (HPLC) or liquid chromatography at critical conditions (LCCC).

4.2.3 Brief view on synthesis of samples

4.2.3.1 Synthesis of multiblock polymers

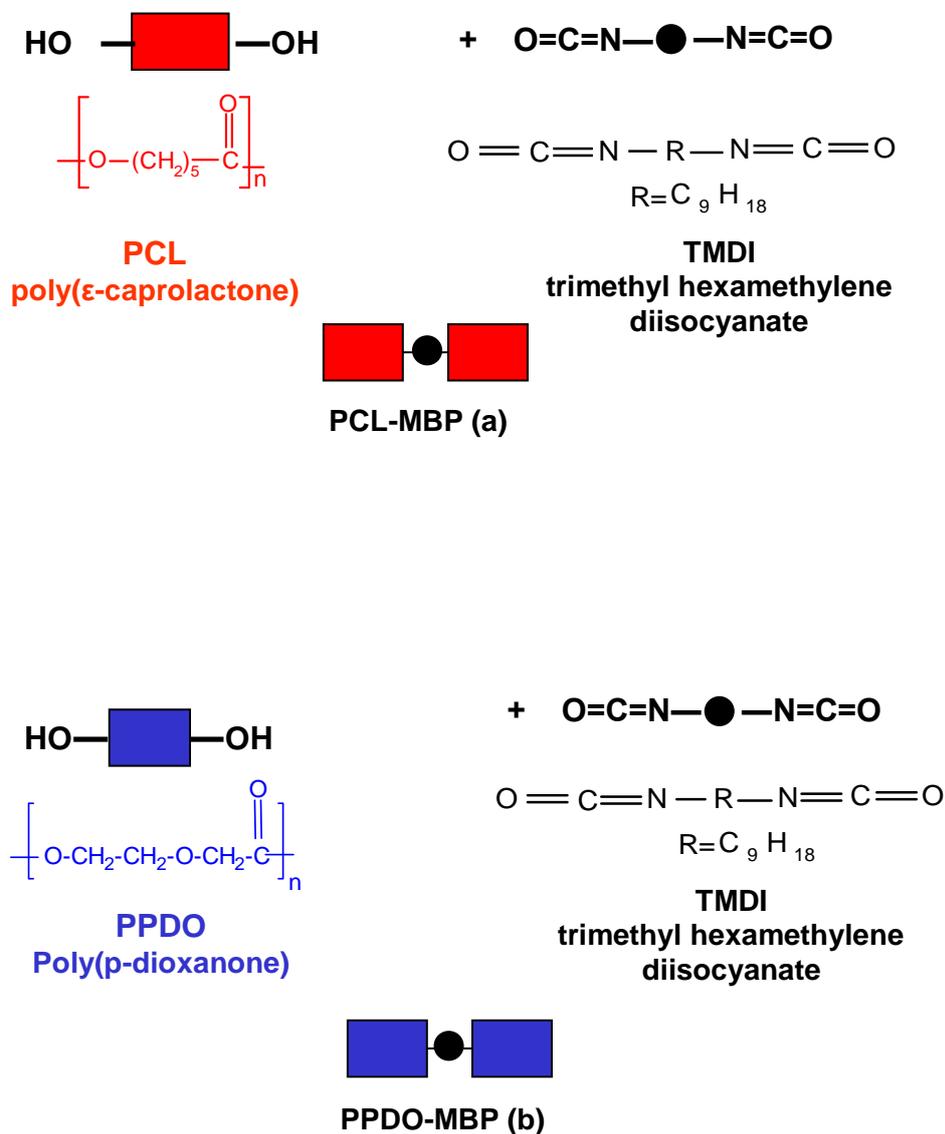


Figure 4.17: Schematic representation of the synthesis multiblock polymers (MBP): (a) PCL-MBP and (b) PPDO-MBP

Fig. 4.17 schematically represents the synthesis and structures of PPDO- and PCL multiblock polymers (PPDO and PCL-MBP). These MBPs had been synthesized at GKSS (Teltow) by separately coupling either poly (*p*-dioxanone) (PPDO) or poly (ϵ -caprolactone) (PCL)-diols with trimethyl hexamethylene diisocyanate (TMDI). MBPs

The chemical composition distribution of the formed multiblock copolymers might have an influence on microscopic properties of the materials. Therefore, the chemical composition distribution of the synthesized multiblock copolymers needs to be examined. Up to now, suitable methods have not yet been commented in the literature for the materials under investigation. Hence, suitable chromatography methods needed to be developed.

4.3 Separation of MBCs by chemical composition distribution using gradient HPLC

The following section is aimed to provide the detailed chromatographic characterization methods for the PPDO-PCL-MBCs. It will be explained step by step how the method development was conducted and how the results have been achieved.

4.3.1 Polymers solubility test

In order to perform liquid chromatography experiments, first at least two different solvents had to be found, in which the two polyester polyols as well as the resulting MBPs and MBCs are completely soluble. Besides solubilizing the different polymers one of the solvents should provide the complete adsorption on the stationary phase while the other should be able to cause the complete desorption from the stationary phase. Therefore, a solvent screening for the different polymers was performed. 1mg of polymer was weighed into a 1.5 mL vial and 1mL of solvent was added. Two samples for each polymer were prepared. One was left for about 1-2 hours at room temperature while the other sample was heated to 50°C for about 30 min. Afterwards, the solutions were gently shaken and visually inspected in order to determine whether or not the polymer has fully dissolved. The results for the different polymers in different solvents are given in Table 4.3.

Table 4.3: Solubility of polymers

Solvent	PCL-Diol ^{a)}		PCL-MBPs ^{b)}		PPDO-Diol ^{c)}		PPDO-MBPs ^{d)}		MBCs ^{e)}	
	RT	50°C	RT	50°C	RT	50°C	RT	50°C	RT	50°C
THF	+	+	-	-	-	-	-	-	-	-
DCM	+	+	+	+	+	+	+	+	+	+
HFIP	+	+	+	+	+	+	+	+	+	+
Acetone	-	+	-	-	-	+	-	-		
CHCl ₃	+	+	+	+	+	+	+	+	+	+
Cyclohexanone	+	+	+	+	+	+	+	+	-	-
ACN	-	+	-	+	-	+	-	+	+	+

a) PCL 2205, PCL 2304, PCL 2402, PCL 2802

b) LP 056

c) PPDO 10, PPDO 5.8

d) LP 065

e) LP 027, LP 070, LP 099, LP 101

Legend: + soluble, – insoluble, RT (room temperature)

From Table 4.3 one can see that the polymers were soluble in hexafluoroisopropanol (HFIP), chloroform (CHCl₃) and dichloromethane (DCM) at room temperature and at elevated temperature. In acetonitrile (ACN) the polymers were soluble only at elevated temperature. After having identified possible solvents the question arose whether these solvents fulfilled the requirements concerning adsorption/desorption of the structures to be separated.

4.3.2 Selection of stationary phase and mobile phase

In order to achieve the separation of multiblock polymers (MBP) and multiblock copolymers (MBC) according to the relative amount of the two polyesters, suitable stationary phases (normal or reversed phase) needed to be identified. Knowing that the repeating units of the polyesters (PCL and PPDO) are less polar than OH and isocyanate groups (N=C=O) one has to use conditions such that the interactions of

the stationary phase with the OH or urethane groups are negligible as compared to the interaction between the stationary phase and the repeating units. Thus, under such conditions, the less polar group (PCL and PPDO) should be absorbed, while the polar groups (OH and isocyanate) should not. Therefore, a reversed phase column (Nucleosil C-18, particles size 5 μ m, and pore diameter 100 \AA , column dimension 250mm \times 4.0 mm) was chosen for further experiments.

As has been shown in Table 4.3, the samples were soluble (at elevated temperature) in four different solvents which are dichloromethane, acetonitrile, chloroform and hexafluoroisopropanol (HFIP). The use of HFIP, however, was less preferred due to its high costs and its toxicity. ACN, CHCl_3 and DCM were thus selected for further chromatographic experiments. Two possible combinations should form suitable mobile phase systems, ACN/ CHCl_3 and ACN/DCM. ACN and DCM (or CHCl_3) were expected to form a pair of adsorption and desorption promoting solvent, and will be referred to in the following as weak and strong eluent components, respectively.

4.4 Chromatography method development

4.4.1 Isocratic measurements of the PCLs, the PPDOs and multiblock polymers (PCL-MBP and PPDO-MBP) in dichloromethane and acetonitrile

Due to the strong dependence of elution volume on molar mass, isocratic adsorption chromatography is usually only possible for non-adsorbing polymers or for weakly adsorbing polymers having a moderate width of molar mass distribution. Since two polymers usually differ in their interaction energies with the stationary phase, it is nearly impossible to separate two chemically different polymers under adsorbing isocratic conditions. Therefore gradient methods need to be applied, which require at least one weak and one strong eluent. To investigate the eluent strength of the selected solvents for the different polymers on the selected stationary phase the isocratic elution behavior of the different polyols and MPBs was investigated. From these experiments eluent conditions allowing for adsorption and desorption of the diols should be extracted.

Isocratic runs using dichloromethane (DCM) as mobile phase were conducted on the selected stationary phase for the different PCL-diols, PPDO-diols and multiblock polymers (PPDO-MBP and PCL-MBP).

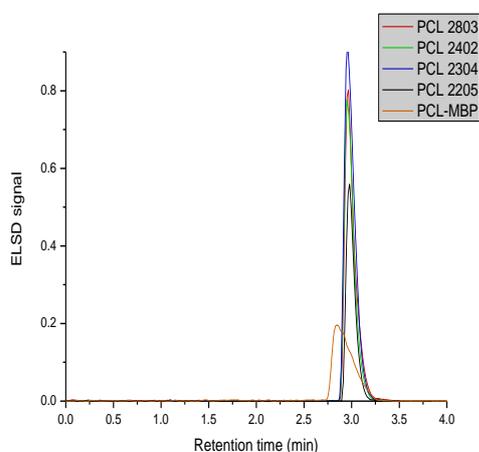


Figure 4.19: Chromatograms of PCLs 2803 (red), 2402 (green), 2304 (blue), 2205 (black) and PCL-MBP (orange) obtained by isocratic runs. Mobile phase: DCM, (Nucleosil C-₁₈, particle size 5 μ m, and pore diameter 100 Å , column dimension 250mm \times 4.0 mm), flow-rate: 1.0mL/min. Detector: evaporative light scattering (ELSD)

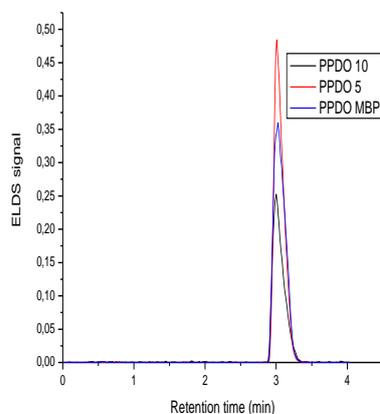


Figure 4.20: Chromatograms of PPDO-10 (black), PPDO-5 (red), PPDO-MBP (blue) obtained by isocratic run. Mobile phase: ACN, (Nucleosil C-₁₈, particles size 5 μ m, and pore diameter 100 Å , column dimension 250mm \times 4.0 mm), flow-rate: 1.0mL/min. Detector: evaporative light scattering (ELSD)

Fig. 4.19 shows the chromatograms of different PCL-diols and PCL-MBP performed isocratically in DCM. For all samples only one peak is obtained. All polymers elute at 2.7-3 min retention time. This indicates that DCM desorbs PCL and PCL-MBP from the stationary phase. Since the polymers elute in the void volume, there is no interaction between the polymers and the stationary phase. Fig. 4.20 shows the chromatograms of different PPDO-diols and a PPDO-MBP performed using the same chromatographic conditions. The PCL-diols, PPDO-diols and the PPDO-MBP also elute in one peak at 3.1 min retention time. This shows that DCM desorbs the PPDO-diols and PPDO-MBP from the stationary phase. Due to the fact that the polymers elute in the void volume, there is no interaction between the polymers and the stationary phase.

The results in Figs. 4.19 and 4.20 show that DCM is a good eluent for PPDO-diols, PCL-diols and for PPDO and PCL-MBP. Therefore DCM might be used as the strong eluent during gradient elution, as it should be desorbed and elute all samples.

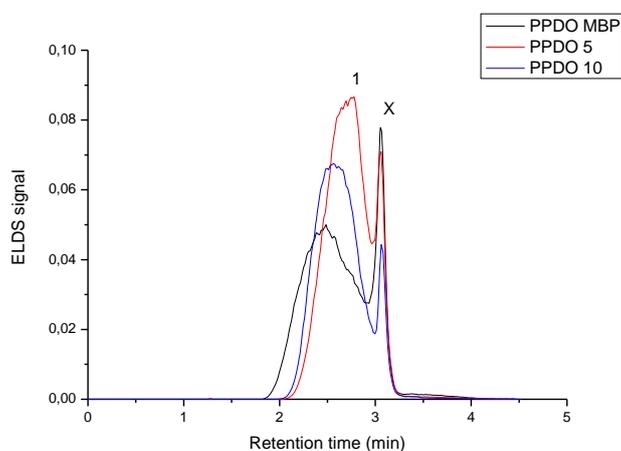


Figure 4.21: Chromatograms of PPDO-10 (blue), PPDO-5 (red) and PPDO-MBP (black) obtained by isocratic runs using ACN as mobile phase. (Nucleosil C-₁₈, particles size 5 μ m, and pore diameter 100 \AA , column dimension 250mm \times 4.0 mm), flow-rate: 1.0mL/min. Detector: evaporative light scattering (ELSD))

Having established conditions allowing for complete desorption of both polyols and the MBPs, the next step in the method development consisted in identifying conditions at which at least one of the components was adsorbed onto the stationary phase. Fig. 4.21 shows the chromatograms obtained from isocratic runs for PPDO-diols and MBPs performed in ACN. PPDOs and PPDO-MBP eluted in two peaks. The main peak 1 eluted roughly at 2.5 min and is assigned to be the polymer peak. Another sharp peak (x) at 3 min was observed in all PPDO-containing samples. The origin of it is unknown at this early stage of the method development. The elution of the polymer before the void volume indicates that PPDO-diols and PPDO-MBP are not adsorbed in ACN or to be more precise a potential weak adsorption is much weaker than the exclusion effect: This means that ACN desorbs the PPDO-segments.

In contrast to the elution behavior of the PPDOs, PCL-diols and PCL-MBPs did not elute at all from the column in pure ACN. The polymers were fully retained within the

stationary phase. This indicates that ACN is an adsorption promoting solvent (weak eluent) for the PCL-diols and PCL-MBP.

Summarizing the above results we can conclude that DCM is a strong eluent for the PPDO-diols and PPDO-MBP as well as for PCL-diols and PCL-MBP because all polymers were eluted from the stationary phase. ACN, however, is a strong eluent only for the PPDO-diols and PPDO-MBPs, while it promotes adsorption (weak eluent) in the case of PCL-diols and PCL-MBPs.

Due to the above mentioned properties of the two eluents they might form a suitable pair of a weak and a strong eluent as required for gradient application. Therefore gradient experiments were performed on the selected stationary phase using gradients of ACN and DCM.

4.4.2 Gradient liquid chromatography of the polymers

As it is widely documented [17,29] that gradient liquid chromatography is capable for separating complex copolymers with regard to their chemical composition. If good solvents are used, which therefore prevent precipitation, the separation mechanism of gradient liquid chromatography is mainly based on the differences in adsorption strength of the copolymers of different chemical composition.

During the gradient liquid chromatography separation the solvent composition is changing gradually with time from a weak to a strong eluent. At the beginning of the gradient the polymer is adsorbed onto the stationary phase due to the weak eluent applied. Depending on chemical composition and molar mass of the copolymer, the polymers will desorb at a certain solvent composition, which depends on their chemical composition. Hence, polymers of different compositions will elute at different retention times and separation occurs.

4.4.2.1 Gradient liquid chromatography of the PCL-diols, PPDO-diols and their multiblock polymers

Since ACN was found to desorb PPDO containing polymers, while the PCL containing polymers were adsorbed, it was expected that a gradient ranging from

ACN to DCM would elute first PPDO-diols and PPDO-MBPs, while PCLs and PCL-MBP containing polymers should be desorbed within the gradient when the DCM content is high enough to desorb the PCL-segments.

In order to test this hypothesis the elution behavior of PPDO-diols, PCL-diols, PPDO-MBPs and PCL-MBPs were investigated by gradient chromatography. The initial mobile phase was ACN and the final mobile phase was DCM. The composition of the mobile phase was linearly changed from 100% ACN to 100% DCM within 10 min and then kept at 100% DCM for 1 min before returning to the initial composition. Finally, re-equilibration of the column with pure ACN was allowed for 5 min. The different steps of the gradient chromatography are given in Table 4.4. The results are illustrated in Figs. 4.22 and 4.23.

Table 4.4: Gradient HPLC mobile phase for the PCLs and PPDOs

Time (min)	Flow-rate(mL/min)	ACN%	DCM%
0	1.0	100	0
10	1.0	0	100
11	1.0	0	100
16	1.0	100	0

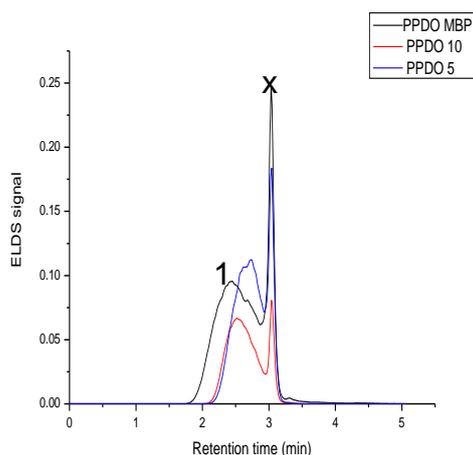


Figure 4.22: Chromatograms of PPDO-diols PPDO-10, PPDO-5 and a PPDO-MBP obtained by gradient elution: stationary phase Nucleosil C₋₁₈, particles size 5 μ m, and pore diameter 100 Å , column dimension 250 mm \times 4.0 mm, 10 min linear gradient from ACN to DCM, flow-rate: 1.0mL/min. Detector: evaporative light scattering (ELSD).

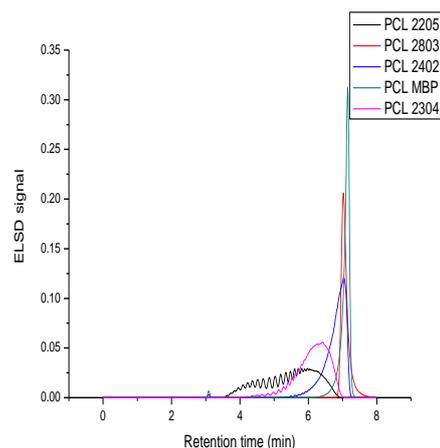


Figure 4.23: Chromatograms of PCL-diols (2803, 2402, 2304, 2205) in order of increasing molar mass, and PCL-MBP last obtained by gradient elution: stationary phase Nucleosil C₋₁₈, particles size 5 μ m, and pore diameter 100 Å , column dimension 250 mm \times 4.0 mm, 10 min linear gradient from ACN to DCM, flow-rate: 1.0mL/min. Detector: evaporative light-scattering (ELSD).

Fig. 4.22 shows the chromatograms of PPDO-10, PPDO-5 and the PPDO-MBP. One can see that all PPDOs eluted before the dead volume of the column. This indicates that PPDOs were not retained within the column. The sharp of PPDO-diols peak in the gradient is similar to the PPDO-diols peak in pure ACN. Since in the gradient the solvent composition is changing gradually with time from a weak (ACN) to a strong eluent (DCM), ACN being a good solvent for PPDO, because it causes no adsorption for PPDO on the stationary phase, this explains why PPDOs elute in pure ACN in gradient. In Fig. 4.22 two peaks are observed for all polymers. The first peak is at 2.25-2.5 min (peak 1) and a second peak at 3 min (peak x). Peak 1 represents only PPDO for the PPDO-10 and 5. For PPDO-MBP, the peak 1 might represent PPDO-MBP, PPDO-diols or a mixture of both. The peak x for all polymers (PPDOs and PPDO-MBP) remains unknown.

Fig. 4.23 shows the chromatograms of PCL-diols and PCL-MBP. Contrary to the PPDO-diols and PPDO-MBPs, the PCL-diols and PCL-MBP elute within the gradient. This can be ascribed to the fact that the PCL-diols and PCL-MBP are absorbed at the initial mobile phase composition onto the stationary phase and were desorbed as the eluent reaches a sufficient solvent strength due to the addition of the DCM. The lower molar mass samples of the PCL-diols show series of peaks which are most probably separated oligomers of different degrees of polymerization. With higher (average) molar mass the samples elute later and the peaks become narrower. This can be attributed to the typical elution behavior of homopolymers. The typical elution behaviour of homopolymers was explained in chapter 3.

Furthermore, the effects of urethane linkages and the end groups existing in the MBPs were examined. One can see that in Figs. 4.22 and 4.23 that PPDO-MBPs elute similar to PPDO-diols in pure ACN and while PCL-MBP elutes similar to PCL-diols within the gradient. The end groups do not contribute to the retention of the polymers.

From the above results two conclusions can be drawn:

- In the same gradient conditions PPDO- and PCL-diols show completely different chromatographic behavior in terms of retention time. PPDO-diols elute before the gradient while PCL-diols elute within the gradient. As a result, a separation according to the chemical composition might be possible by gradient chromatography.
- Under the chromatographic conditions given, PPDO-MBPs elute in the same range as PPDO-diols before the gradient i.e. without any retention in pure ACN. PCL-MBPs elute within the gradient in the same retention range as PCL-diols of high molar mass. Therefore, it is clear to state that the retention of the polymers is governed by the polyester components and the effects of the urethane linkage and functional end groups present on the MBPs are negligible.

4.4.2.2 Gradient liquid chromatography of multiblock copolymers

After the chromatographic conditions had been developed, allowing separation PCL- and PPDO-MBPs, thus differentiating the different polyesters, the question arose whether these conditions are suitable to separate MBCs according to chemical composition. Thus, MBC were analyzed using the same chromatographic conditions. The chromatograms obtained for selected samples are represented in Fig. 4.24.

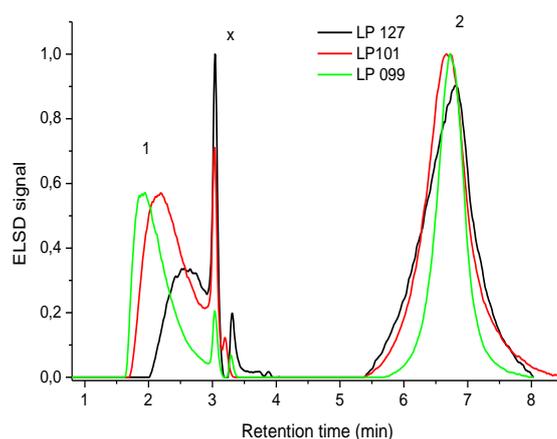


Figure 4.24: Chromatograms of gradient HPLC separations of different multiblock copolymers. Mobile phase: ACN-DCM, stationary phase Nucleosil C₋₁₈, particle size 5 μ m, and pore diameter 100 Å , column dimension 250 mm \times 4.0 mm, Gradient: ACN to DCM linear in 10 min, flow-rate: 1.0mL/min, Detector: evaporative light scattering (ELSD).

Figure 4.24 represents the chromatograms of gradient HPLC of different multiblock copolymers (LP 099, LP 127 and LP 101). The chromatograms of the MBCs show two well separated main peaks (1 and 2). Peak 1 elutes in SEC mode where PPDO-diols and PPDO-MBP elute and peak 2 elutes within the gradient at same range of retention times (6-8min) where PCL-diols and PCL-MBP elute. Additionally a sharp peak (x) close to the dead volume is observed. The origin of this peak x is related to the presence of PPDO, since it was not observed in the absence of PPDO-components.

For segmented copolymers having an adsorbing block it can be expected that the retention in gradient chromatography should essentially be determined by the

adsorbing block, here the PCL. The PCL and the block copolymers should elute in two distinct peaks. This is because the block copolymers being made of part of PPDO-PCL should adsorb less than pure PCL. As a result, the block copolymer should elute before the pure PCL component. Unfortunately, this is not the case in Fig. 4.24 where only one peak elutes within the gradient. Therefore, based solely on the chromatographic behavior, it is difficult to say whether peak 2 contains the block copolymers or not.

From the above results it appears as if the MBCs contain a significant amount of PPDO-diols and/or PPDO-MBP

4.4.3 Liquid chromatography under critical conditions for PCL

In order to clarify whether the block copolymers and PCL-MBP or PCL-diols co-elute within peak 2 of the gradient chromatography, chromatography under critical conditions for PCL was applied. At critical conditions (LCCC) of one block, the block is "chromatographically invisible", i.e. its molar mass does not influence the retention. And the retention of the diblock copolymer is solely determined by the other visible block [17, 21-23, 29, 50-51]. Despite the controversy as to the precision of the method, there is a consensus that LCCC can estimate individual block length copolymers reasonably [52-54].

For two component triblock copolymers, there can exist another variation in chain architecture, i.e., ABA or BAB type. If they have similar molar mass and composition, can we distinguish them by chromatography? Different possibility can be discussed about the influence of polymer architecture on the LCCC retention behavior of AB, ABA and BAB type block copolymers. Under the critical conditions of B block, retention of AB and BAB follows the normal LCCC behavior, and one can measure the molar mass of A block by LCCC while the elution behavior of ABA depends on the relative size of B block [22, 53, 55-57]. If block B length were long, LCCC analysis would not provide the correct molar mass of 2A [50-51].

Aiming to perform the separation according to the chemical composition of the components, a reversed phase (Nucleosil , particles size 5 μ m, and pore diameter 100 \AA , column dimension 250mm \times 4.0 mm) column was selected where the less polar component PPDO compare to PCL component should not be absorbed and the polar groups (OH and isocyanate) should not play a role on the retention. After that it was necessary to find two suitable solvents which will form the mobile phase. As already explained above, one solvent should cause the complete adsorption of PCL on the stationary phase and another one should promote the complete desorption of PCL from the stationary phase. For this task DCM/ACN were selected. Similar to the explanation on page 28 in section 4.1.1 and by using the formula 4.1 the critical composition can be estimated to be 78%/22% DCM/ACN. On the basis of the estimated critical composition, isocratic experiments were performed at the estimated composition of 78%/22% ACN/DCM. The results show that the higher molar mass PCL-diols elute earlier than the lower molar mass ones. This elution behavior indicates SEC-like elution behavior. Therefore the next experiment was conducted at a slightly higher content of ACN. As can be seen in Fig. 4.26 LAC-like elution order was observed, which resulted in an additional experiment performed using an eluent composition of 76%/24% ACN/DCM and finally PCL-diols of higher and lower molar mass elute almost at the same retention time. Accordingly, this shows critical conditions.

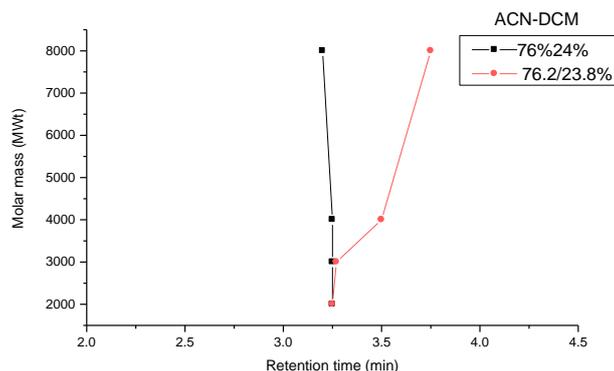


Figure 4.26: Dependence of retention time on molar mass of PCL-diols (2, 3, 4 and 8 kg/mol), mobile phase: ACN-DCM, composition: 76%/24% for LCCC (black squares) where retention is independent of the molar mass and 76.2%/23.8% for LAC (red circles) where the PCL-diols show increasing elution times with increasing molar mass.

Fig. 4.26 shows the graphic representation of the dependence of retention time and molar mass of the PCL-diols. The red curve obtained using an eluent composition of 76.2%/23.8% ACN/DCM shows increasing elution time with increasing molar mass (LAC-like elution behavior), while at an eluent composition of 76%/24% (black curve) all PCL-diols elute almost at the same retention time independent of their molar mass. This indicates critical conditions for PCL.

Having determined critical conditions for PLCs, the elution behavior of PPDO-diols, PPDO- and PCL-MBP were investigated. The results are illustrated in Figs. 4.27 and 4.28.

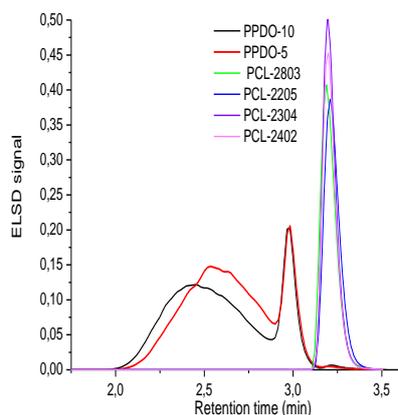


Figure 4.27: Chromatograms of PPDO (Red: 5kg/mol, Black: 10kg/mol,) and PCL-diols (Green: 8kg/mo, Blue: 2kg/mol, Violet: 3kg/mol, rose: 4kg/mol) obtained at critical conditions for PCL. Mobile phase: ACN-DCM (76%/24% v/v). Stationary phase Nucleosil C₋₁₈, particles size 5 μ m, pore diameter 100 Å , column dimension 250 mm \times 4.0 mm). Flow-rate: 1.0mL/min, Detector: evaporative light scattering (ELSD)

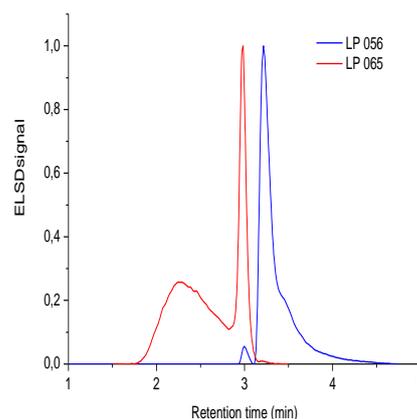


Figure 4.28: Chromatograms of the multiblock polymers samples (Blue: 59kg/mol and Red 19Kg/mol) obtained at critical conditions for PCL. Mobile phase: ACN-DCM (76%/24% v/v). Stationary phase Nucleosil C₋₁₈, particles size 5 μ m, pore diameter 100 Å , column dimension 250 mm \times 4.0 mm). Flow-rate: 1.0mL/min, Detector: evaporative light scattering (ELSD)

Fig. 4.27 shows the chromatograms of PPDO- and PCL-diols while Fig. 4.28 shows the chromatograms PPDO- and PCL-MBP at critical conditions for PCL. One can see that PPDO-diols and PPDO-MBP elute before the dead volume of the column. This indicates weaker interaction strength of PPDO-units as compared to PCL and no interaction of end groups with stationary phase. PCL-MBP elutes at the same retention time (at 3.2 min) as PCL-diols indicating the urethane linkages and functional end groups present on PCL-MBPs are minor importance.

4.4.4 Investigation of MBC at critical conditions of PCL

After having established critical conditions of PCL, the MBCs were investigated. Under the selected conditions the PCL-units should not influence the retention. As

has been verified above, polar end groups and urethane linkages should also not affect the elution behavior. Thus, the retention should be determined only by PPDO units. Typical chromatograms of MBCs are given in Fig. 4.29.

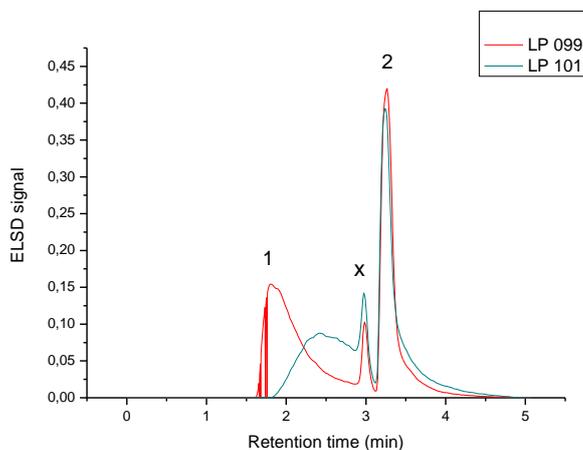


Figure 4.29: Chromatograms of the selected MBC-samples obtained at critical conditions for PCL. Mobile phase: ACN-DCM (76%/24% v/v). Stationary phase Nucleosil C-18, particles size 5 μ m, and pore diameter 100 Å , column dimension 250mm \times 4.0 mm. Flow-rate: 1.0mL/min. Detector: evaporative light scattering (ELSD).

A pure MBC is expected to result in one peak. As can be seen in Fig.4.29 the presence of peak 2 indicated the presence of PCL-units. However, unexpectedly three peaks 1, x and 2 are observed in all chromatograms. Based on the elution volume and the pattern of PPDO-10, PPDO-5 and PPDO-MBP (Figs.4.27 and 4.28), peak 1 is assumed to result from a PPDO-diol, and/or a PPDO-MBP and/or a block copolymers, because they are expected to show weaker interaction with the stationary phase. Peak 2 elutes at the same retention time as PCL-diols and PCL-MBP. For this reason, it has to be assigned to pure PCL and/or PCL-MBP. This leads to the assumption that the peak x (3 min) cannot be assigned as part of the polymer structure. This peak might be due to impurity from the catalyst used during the chemical reaction.

From the above results it appears as if the MBCs contain a significant amount of PCL-diols or PCL-MBP.

According to the two chromatographic results it is very difficult to say if the block copolymer is present or not. The gradient chromatography and LCCC have showed no indication for the block copolymer. But it can be hypothesized that, if the block copolymer exists in the multiblock copolymers, in the gradient chromatography a block copolymer and the corresponding homopolymer of the block which is stronger adsorbed are expected to elute at similar elution volumes. Thus, the second peak of the gradient chromatography might consist of purely PCL containing structures and/or the true multiblock copolymer. In this case the PPDO containing structures in the block copolymer should be very low. In LCCC, since we are under LCCC of PCL, PPDOs and MBCs are expected to elute in SEC-mode before the void volume while PCL is expected to elute at the void volume. Based on the elution volumes the first peak, eluting before the void volume, is assumed to result from PPDO-diols, and/or PPDO-MBPs and/or MBCs, because they are expected to elute in SEC-mode. The second peak elutes at the void volume identical to the PCL-diols and PCL-MBPs. Thus, this peak has to be assigned to "pure" PCL and/or PCL-MBP. Accordingly, the existence of the block copolymer cannot be excluded based on the experiments so far. In addition, the above unexpected results were derived completely from the retention times of the different peaks and theoretical expectations. However, since the results were unexpected, alternative methods were applied to prove the above results.

4.5 Characterization of different peaks from gradient chromatography

In order to answer the questions whether peak 2 of the gradient chromatography and peak 1 in LCCC contain MBCs attempts were undertaken to identify the chemical composition of the different peaks by off-line FTIR, Py-GC-MS and proton NMR.

4.5.1 Fourier-Transform Infrared Spectroscopic (Attenuated Total Reflectance) Analysis

As has been shown in the chromatographic analyses it is possible to differentiate PPDO- and PCL-containing polymers. Therefore, peak 1 and peak 2 from gradient chromatography of MBC LP 070 were manually fractionated in F1 and F2. After collection of the fractions the solvent was removed. The residue was re-dissolved in

ACN and put as a solution on the ATR, allowing the solvent to evaporate. The FTIR spectrum of each fraction was recorded. According to the interpretation of the chromatographic separation, peak 1 is expected to contain PPDO, while peak 2 should be composed of PCL. Therefore, the FTIR spectrum of F1 was compared to that of PPDO-MBP in Fig. 4.30 while the FTIR spectrum of F2 was compared to that of PCL-MBP in Fig. 4.31.

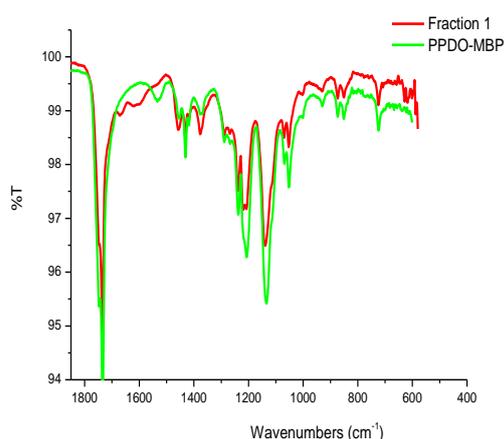


Figure 4.30: Comparison of the FTIR spectrum of Fraction 1 from gradient chromatography of MBC LP 070 (red) with the FTIR-spectrum of PPDO-MBP (green)

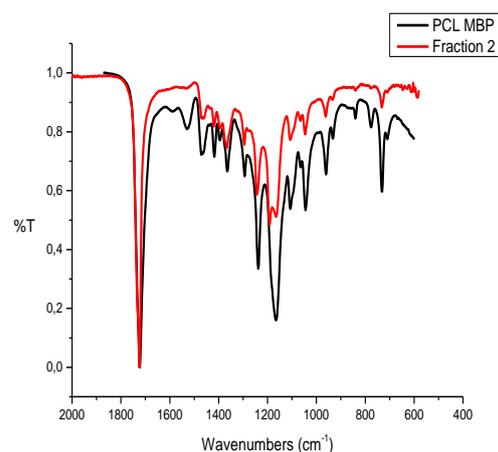


Figure 4.31: Comparison of the FTIR spectrum of Fraction 2 from gradient chromatography of MBC LP 070 (red) with the FTIR-spectrum of PCL-MBP (blue)

As can be seen in Fig. 4.30 the FTIR spectra of F1 of MBC LP 070 and of PPDO-MBP are very similar. The characteristic absorption bands of PPDO are observed at $872\text{-}846\text{ cm}^{-1}$ indicating the presence of PPDO-structures. However, the characteristic absorption band for PCL/PCL-MBP at 1161 cm^{-1} is absent in the spectrum of fraction F1, indicating that this fraction does not contain PCL, or that its amount is too low to be identified by FTIR. This confirms the conclusion from gradient chromatography that the first peak of MBC LP 070 is assigned to be a PPDO-rich material.

Based on the chromatographic behavior fraction 2 in gradient chromatography might contain block copolymer. However, the comparison of the FTIR spectra of fraction 2

of MBC LP 070 with that of a PCL-MBP (Fig. 4.31) reveals the characteristic bands of PCL at 1161cm^{-1} , while the characteristic absorption bands for PPDO containing structures at $874\text{-}851\text{cm}^{-1}$ are absent. Accordingly, this suggests that fraction 2 of MBC LP 070 from gradient chromatography consists mainly of PCL-units. If MBCs are present at all, they have to have a very low content of PPDO.

After identifying the nature of peaks 1 and 2 from gradient chromatography by means of FTIR, the next step was to determine the composition of PPDO in each peak by means of coupling LC-FTIR. To make experiments possible, it was first necessary to check if the PPDO average composition determine by SEC-FTIR slice by slice as illustrated in Fig.4.32 is in an agreement with the PPDO composition given by supplier.

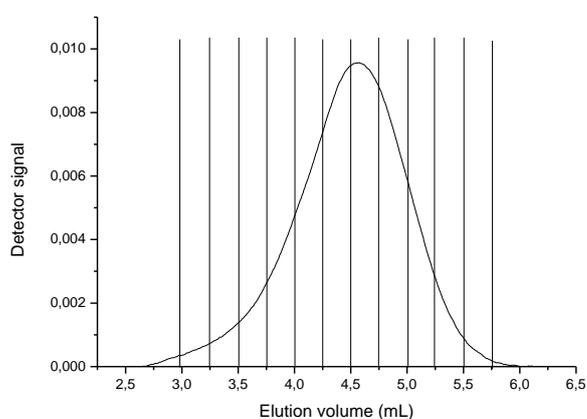


Figure 4.32: Fractions of SEC-FTIR

One of the benefits of coupled SEC-FTIR is the ability to collect the total amount of the sample on one spot. SEC allows obtaining one peak which contains the total material of the sample. By examining the compositions of the sample slice by slice, will probably give the true content of PPDO compared if the measure was conducted on the bulk sample. Once this is proven the PPDO average composition determine by SEC-FTIR slice by slice is in an agreement with the PPDO composition given by supplier, one can use the same procedure to determine the composition of PPDO in fractions 1 and 2 of the gradient chromatography of the MBCs. For this FTIR required a suitable calibration curve.

In order to construct a calibration curve allowing to calculate the chemical composition of the MBCs, solutions of PPDO-MBP and PCL-MBP at different compositions (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 wt%) were prepared in DCM (total concentration approx. 1.5 mg/mL). For the calibration, the LC-transform system was used. The principle of LC-FTIR was explained in chapter 3. The polymer materials were directly sprayed onto the Ge-disc without prior separation (no column) in order to obtain the same mixture on the Ge-plate. Each solution was measured two times to ensure the reproducibility of the result. Afterwards spectra of each solution were recorded and analyzed by FTIR software. To be able to determine the PPDO content in the MBCs samples, the bands at 1146 cm^{-1} and at 1178 cm^{-1} were selected. Before determining the peak heights, the baseline was selected by purpose between 2204 – 800 cm^{-1} in order to cover the range of interest, and was kept identical for all samples. For each solution, the peak heights (I_1) at 1146 cm^{-1} and the peak height (I_2) at 1178 cm^{-1} were determined. The ratio I_1/I_2 was determined by using equation:

$$r = \frac{I_{1\text{copolymer}}}{I_{2\text{copolymer}}} = \frac{\Sigma I_1 \text{ fraction SEC}}{\Sigma I_2 \text{ fraction SEC}} \quad 4.1$$

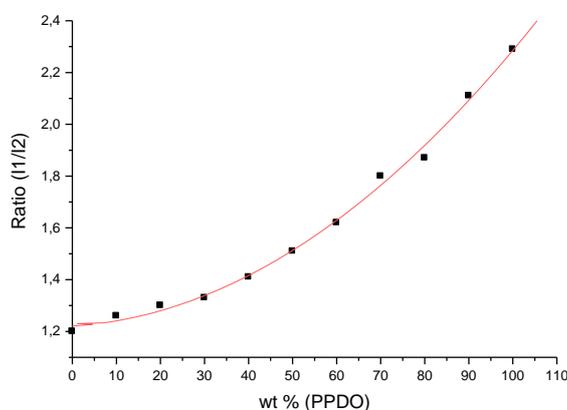


Figure 4.33: Calibration curve for relation between PPDO composition and peak height

In Fig. 4.33 one can see that a good correlation between the data points and the fitted curve is obtained ($R^2=0.99$). The third degree polynomial function was used for fitting the curve.

Having established the calibration curve, it was possible to perform the SEC-FTIR experiment on the MBCs. Thus, MBC samples were dissolved in chloroform (~1.5 mg/mL) and separated by SEC. The eluate was sprayed on the Ge-plate using the LC-transform interface. Afterwards, series of FTIR spectra was recorded and analyzed by FTIR software. Two runs were made for each sample in order to prove the validity of the results. For each MBC the peak heights (I_1) at 1146 cm^{-1} and the peak height (I_2) at 1178 cm^{-1} were determined slice by slice. And the ratio I_1/I_2 was determined by using the equation 4.1. By using the calibration curve (Fig.4.33), the PPDO contents of the MBCs were determined. In Table 4.5, these data are compared with the expected PPDO contents from the MBCs synthesis. This comparison is graphically represented in Fig. 4.34 as well.

Table 4.5: Comparison between PPDO contents of the MBCs measured by SEC-FTIR and PPDO content from synthesis

Samples	%PPDO measured by SEC-FTIR (wt%)	%PPDO from Synthesis (wt%)
LP 099	57	50
LP 101	50	50
LP 102	46	50
LP 103	56	50
LP 126	67	60
LP 127	62	60
LP 166	48	50

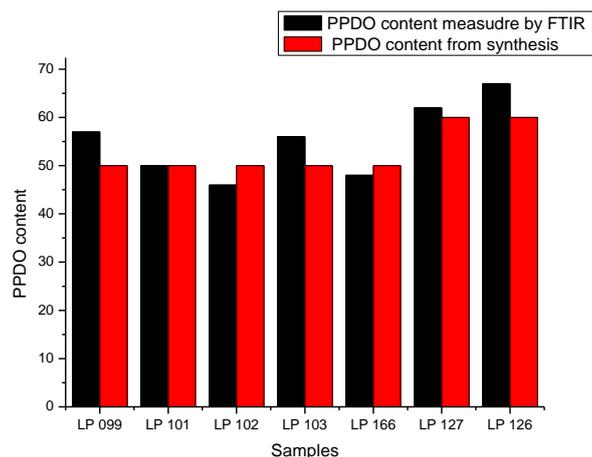


Figure 4.34: Graphic comparison between the PPDO content of the MBCs measured by SEC-FTIR with the ones from synthesis

From table 4.6 and Fig. 4.34 one can see that good agreement is observed between PPDO content measured by FTIR and PPDO content from synthesis. Thus, the FTIR analysis based on the selected peak positions and on the established calibration curve allows the determination of compositions of the MBCs.

Encouraged by these results, the composition of PPDO in peak 1 and 2 of the gradient chromatography can then be determined by using the same procedure.

4.5.2 Determination of composition in peaks 1 and 2 from gradient chromatography of the MBCs by LC-FTIR spray device.

After checking that the PPDO average composition of the MBCs obtained by SEC-FTIR matches with the PPDO average composition from synthesis, one can determine the PPDO contents of the different MBCs in peak 1 and 2 of gradient chromatography. After separation by gradient chromatography, the samples were sprayed on the Ge-plate using the LC-transform interface. Afterwards, a series of FTIR-spectra was recorded and analyzed for each MBC. The peak heights (I_1) at 1146 cm^{-1} and the peak height (I_2) at 1178 cm^{-1} were determined separately slice by slice for peak 1 and 2 of gradient chromatography. The ratio I_1/I_2 was determined by using the equation 4.1. From the calibration curve (Fig. 4.33), the PPDO contents in peak 1 and peak 2 of gradient chromatography of different MBC were determined as illustrated in Table 4.6.

Table 4.6: PPDO content in the peaks 1 and 2 of gradient chromatography of the MBCs measured by LC-FTIR spray device.

Samples	Fraction 1 (wt%)	Fraction 2 (wt%)
LP 099	96	0
LP 101	89	0
LP 102	80	0
LP 103	83	0
LP 127	93	0

Table 4.6 shows the PPDO content in the peaks 1 and 2 of the gradient chromatography of different MBCs measured by LC-FTIR. All MBCs showed more than 80 % (wt %) of the PPDO content in the peak 1, whereas in the second peak of the gradient chromatography of the MBCs no PPDO was found. Thus, the peak 1 of the gradient chromatography of the MBCs consists for the most part of the PPDO-units and a small content of PCL-units (Table 4.6). These results are in agreement with those obtained by FTIR, where the peak 1 of the gradient chromatography indicated a large number of PPDO, while no PPDO was observed in the peak 2.

The experiments on the identification of the peaks conducted so far qualitatively identified the components in the two peaks resulting in gradient chromatography. It was shown that the two peaks significantly differ in their chemical composition, i.e. a significant heterogeneity is observed for the complete sample. This, however, raises the question, whether there exists also a variation in chemical composition across the individual peaks. In order to answer this question it is required to gain chemical information on chemical composition across the chromatographic peaks. Therefore

LC-FTIR experiments were conducted. As typical example of such an experiment, the investigation of MBC LP 101 will be discussed.

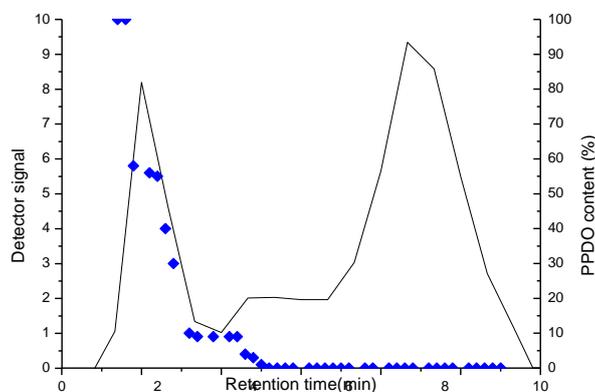


Figure 4.34: shows gradient chromatography separation of MBC LP 101 (black curve) together with ratio of peak (blue squares) across the peaks. Mobile phase: ACN-DCM, (Nucleosil C-18, particle size 5 μ m, and pore diameter 100 \AA , column dimension 250 mm \times 4.0 mm), gradient: ACN-DCM linear at 10 min, flow-rate: 1.0mL/min, Detector: IR

Fig. 4.34 shows the Gram-Schmidt chromatogram for the chromatographic separation of MBC LP 101 (black curve) together with the chemical compositions (blue squares) across the chromatography peaks. As expected the chemical composition analysis (PPDO content) shows a large and continuous variation of the chemical composition along the elution profile. The chemical composition in peak 1 starts at 100% of PPDO content and decreases until 0% in peak 2. This result is consistent with the result in Table 4.6 where it was shown that peak 1 of the gradient chromatography of the MBCs is principally made of PPDO and the peak 2 of the gradient chromatography contains no PPDO. Here, one has to hypothesize that the peak 2 of the gradient chromatography of the MBCs might not have completely the PPDO containing structures or might have low PPDO containing structures which cannot be detected due to the detection limit of the FTIR. Thus, the absence of PPDO containing structures in peak 2 of the gradient chromatography of the MBCs excludes totally the existence of block copolymers.

Since the identification of the gradient chromatography peaks by FTIR has produced some unexpected results, it is wise to explore other techniques which might be more sensible than FTIR. For this pyrolysis gas chromatography mass spectroscopy (Py-GC-MS) was used.

4.5.3 Pyrolysis Gas Chromatography Mass Spectroscopy (Py-GC-MS)

The identification of the gradient chromatography peaks by means of FTIR did not give any indication for the presence block copolymers. FTIR might have a problem of sensitivity if the content of block polymers in the samples is low. For this, Py-GC-MS might be more sensitive for the task than FTIR. A typical system of Py-GC-MS consists of a low dead-volume pyrolyzer, a high resolution capillary GC and a detector. Polymers are thermally degraded at high temperatures in the pyrolyzer and the volatile pyrolysates are swept into the high resolution GC for separation and detection by a mass spectrometer. One advantage of using Py-GC-MS is that even small quantities of material (less than 100 μ g) can be detected and identified.

4.5.3.1 Strategy of identification

In order to identify the individual peaks from gradient chromatography by means of Py-GC-MS, it was necessary to find out whether the two polyester components can be separated by Py-GC-MS. Once the separation is achieved, one can then proceed on the identification of each eluted peak. Therefore, first a mixture of 75% of PPDO-MBP and 25% of PCL-MBP was prepared and pyrolyzed at 450°C. Py-GC-MS was run in total ion chromatogram (TIC) mode. The TIC is constructed by summing the total of ion abundances coming off the GC at a particular time. By determining the elution time of a standard from GC using TIC mode, it is possible to make the initial identification of the compound of interest. Thus, the total ion chromatogram (TIC) resulting from Py-GC-MS of this mixture is illustrated in Fig. 4.36.

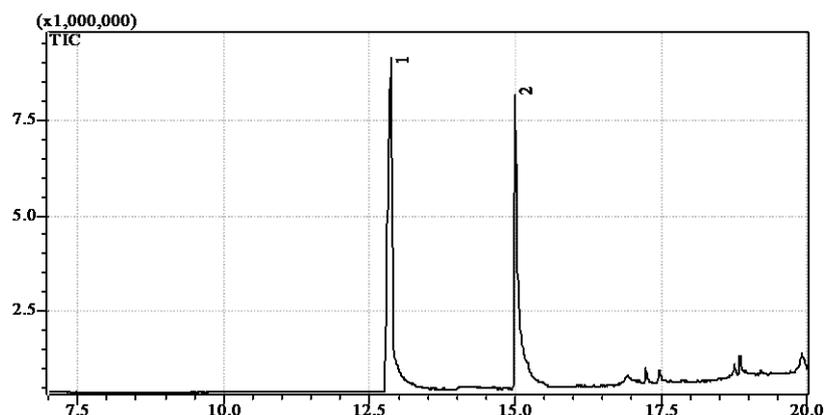


Figure 4.36: Total ion chromatogram (TIC) resulting from a mixture of PPDO-/PCL-MBP (75%/25%)

Two peaks labeled 1 and 2 can be observed at retention times of approximately 13 and 15 min. The pyrolysis temperature was 450°C and the temperature program was set a 60°C. The degradation mechanisms was done simply unzip at pyrolysis temperatures to produce reproducible fragmentation products characteristic of the original polymer. From the relative intensities, one can see that the factor response differs in both polymers. Since the detection takes place by a mass spectrometer in the scanning mode, the mass spectra of the peaks can be extracted.

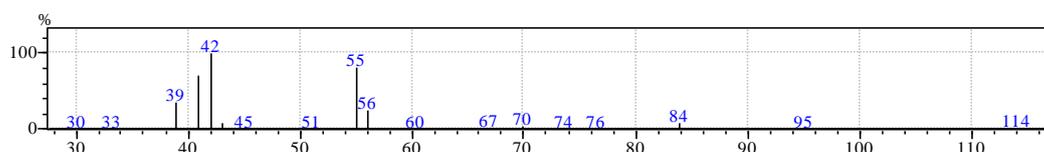


Figure 4.37: Mass spectrum of peak labeled number 2 in figure 4.36

Fig. 4.37 shows the mass spectrum of the peak labeled 2 (15 min) in Fig. 4.36. By running a data base search using the mass spectrum of peak 2, the structure and the mass spectrum of ϵ -caprolactone was found as illustrated in Fig. 4.38. This indicates that the peak labeled 2 in Fig. 4.36 is assigned to ϵ -caprolactone.

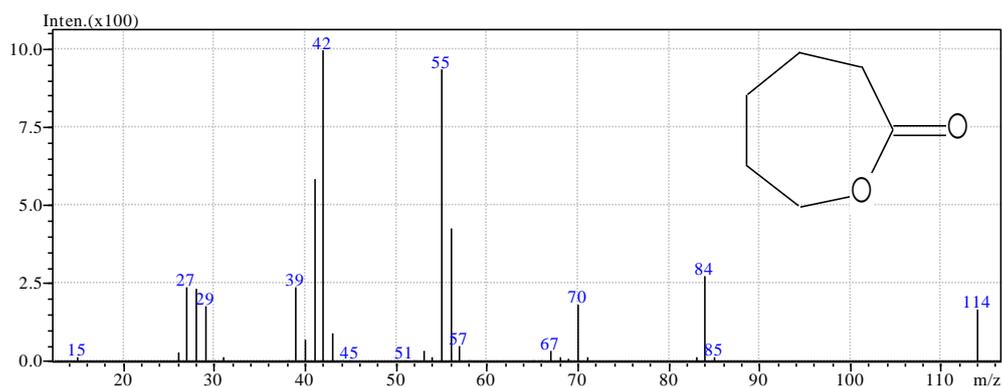


Figure 4.38: Mass spectrum of peak ε-caprolactone obtained from library search.

The mass spectrum of the peak labeled number 1 in Fig. 4.36 is given in Fig. 4.39.

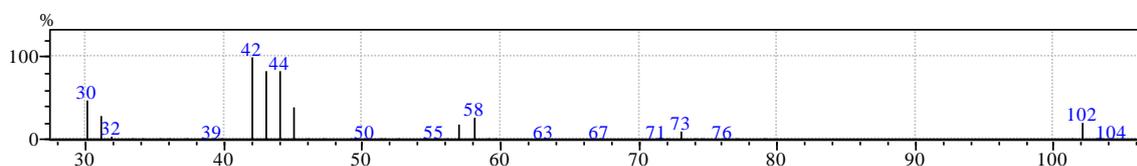


Figure 4.39: Mass spectrum of peak number 1 in Figure 4.36

Contrary to the mass spectrum of the peak labeled 2 in Fig. 4.36 (15 min), a suitable mass spectrum for comparison of the peak labeled 1 in Fig. 4.36 (13 min) was not found from library search. By pyrolyzing a pure PPDO only one peak elutes at around 13 min. The mass spectrum of this peak was determined and was identical to the mass spectrum of the peak labelled number 1 in Fig. 4.36. Accordingly the peak labeled number 1 in Fig. 4.36 represents p-dioxanone (PPDO).

Since the identification of the mixture has given reliable results, the same method can be performed to identify the components in different MBCs.

4.5.3.2 Pyrolysis of the multiblock copolymers

Having identified the different retention times of characteristic pyrolyzates for PPDO- and PCL, the characterization of the MBCs without prior separation in liquid chromatography was conducted by Py-GC-MS. The purpose of this investigation was to determine both the chemical composition of peaks and to evaluate the

content of each component. As an example, the TIC of MBC LP 127 is illustrated in Fig. 4.40.

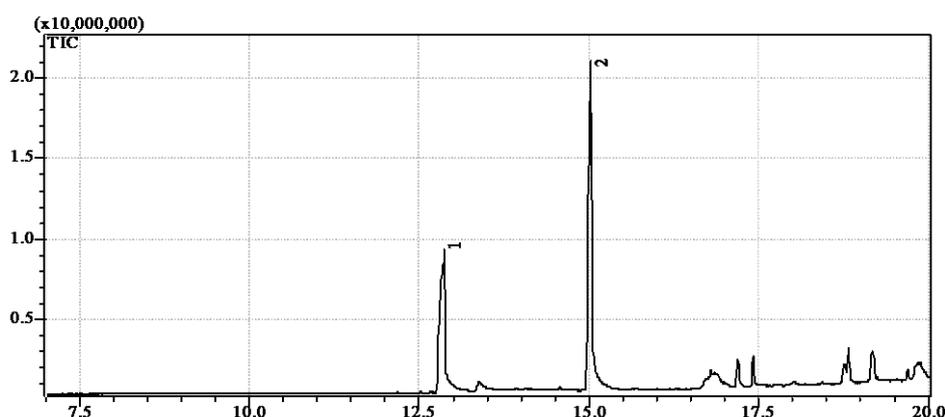


Figure 4.40: Total ion chromatogram of MBC LP 127

Similar to the mixture of the two MBPs above, two peaks were observed at 13 and 15 min, respectively. In addition, the mass spectra of the peaks 1 and 2 from MBC LP 127 are identical to the respective peaks of the MBP-mixture. These similarities are strong evidence to state that the peaks at 13 and 15 min of MBC LP 127 can be assigned to p-dioxanone (PPDO) and ϵ -caprolactone (PCL), respectively. Other MBC samples provided similar results than the MBC LP 127. From Py-GC-MS results it is difficult to conclude that the MBCs contain a block copolymer or not. This indicates that MBC might be made of the two MBP (PPDO/PCL-MBP).

After identifying the component in different MBCs it was then possible to determine the average composition of PCL in different MBCs. To make this possible, the suitable calibration needs to be constructed.

Similar to LC-FTIR a calibration curve needs to be constructed for quantification of the composition. The calibration curve was constructed by preparing the solutions of different compositions (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 (wt%) of PPDO-MBP/PCL-MBP in DCM. Each solution was pyrolyzed by injecting the solution two times (5%, wt% error) to obtain information on repeatability of the results. The TIC for all solutions showed two peaks at 13 and 15 min. The first peak at 13 min belongs to p-dioxanone and the second peak at 15 min had been identified as ϵ -caprolactone. The calibration curve given in Fig. 4.41 was

constructed by plotting the percentage area of ϵ -caprolactone peak versus PCL composition of the mixture.

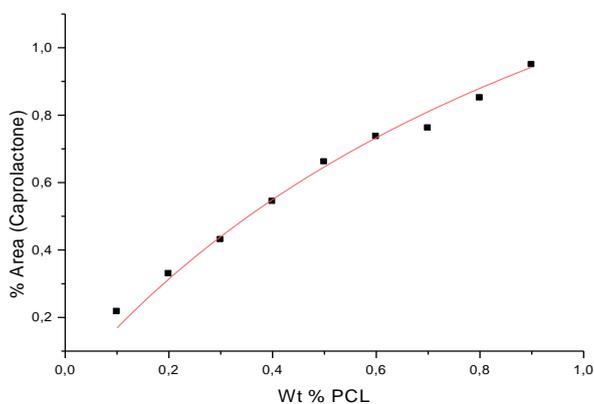


Figure 4.41: Dependence of area percentage of PCL peak in pyrolysis GC-MS versus blend composition.

In this Fig. 4.41 one can see that the correlation between the data points and the fitted curve is obtained ($R^2=0.99$). The third degree polynomial function was used for fitting the curve. As expected for pyrolysis GC-MS, the calibration curve is non linear which means that the response factor differ for both polymers in pyrolysis GC-MS. If one assumes the fact that the peak areas of the PPDO and/or of the PCL peaks in the pyrolysis to the sample injected are proportional then can be described the relative area of PCL as:

$$Area(PCL) = \frac{w}{w(1-B) + B} \quad 4.2$$

where Area (PCL) is the area of PCL peak in the Total ion chromatogram (TIC) that, w is PCL compositions (10-100 wt%) and $B = k^*PPDO/k^*PCL$ (2.05) is the relationship of the factor response of PCL and PPDO.

4.5.3.3 Determination of PCL content in the multiblock copolymers

Having established the calibration curve the different MBCs were investigated in order to support the validity of the method. Each MBC was pyrolyzed two times (3% wt% error). Similar to the mixture, two peaks were obtained at 13 min p-dioxanone

and 15 min ϵ -caprolactone for each MBC. The average composition was determined using the experimentally determined percentage peak area of ϵ -caprolactone and the above established calibration curve. In Table 4.7 the PCL contents of different MBCs measured by Py-GC-MS were compared with those from synthesis. This comparison is graphically represented in Fig. 4.42 as well.

Table 4.7: Comparison of the average PCL contents of the MBCs measured by Pyrolysis GC-MS with the ones expected from synthesis.

Samples	PCL content Py-GC-MS (%wt)	PCL content from GKSS (%wt)
LP099	49	50
LP101	45	50
LP102	52	50
LP103	53	50
LP126	48	40
LP127	60	40
LP 166	56	50

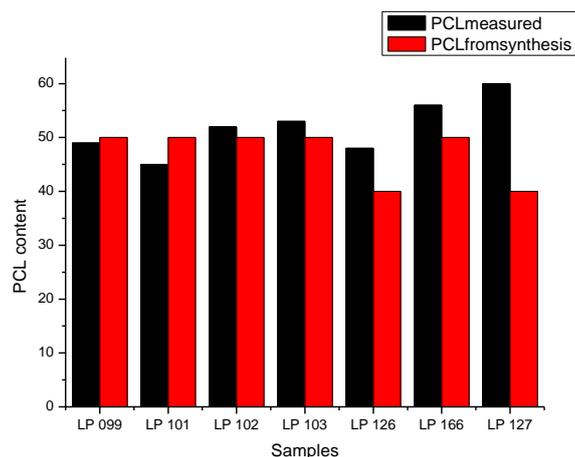


Figure 4.42: Graphic comparison between the PCL content of the MBCs measured by pyrolysis GC-MS with the ones from synthesis.

One can see that the PCL contents of the MBCs measured by pyrolysis GC-MS are almost in perfect agreement with the PCL content expected from synthesis. This result matches very well with the results obtained for LC-FTIR. From pyrolysis results one exception is observed for MBC LP 127 where a deviation of 20% is observed. This lets to the assumption that the composition from the synthesis as given by the supplier might be incorrect. Indeed, raising the question to the supplier of the sample revealed that only incomplete information of the sample is available.

Since the method used for the comparison of the PCL content measured by Py-GC-MS and PCL content from synthesis has shown meaningful agreement, now it is possible to investigate the composition of PPDO in peaks 1 and 2 from gradient chromatography of the MBCs.

4.5.3.4 Pyrolysis of the fractions 1 and 2 from gradient chromatography

After pyrolysis GC-MS on a mixture of PPDO/PCL-MBP (Fig. 4.36) and on MBC LP 127 (Fig. 4.40), it was possible to apply the method to the fractions of the MBCs from gradient chromatography. This experiment was done in order to check if the different peaks are pure PPDO and PCL or contain mixtures of both components. In addition the compositions of each peak need to be determined. Thus, the peaks 1 and 2 of the MBCs from gradient chromatography were manually fractionated. Afterwards, the

fractions were separately pyrolyzed. As examples, the TICs of fraction 1 and fraction 2 from gradient chromatography of MBC LP 127 are shown in Figs. 4.43 and 4.44.

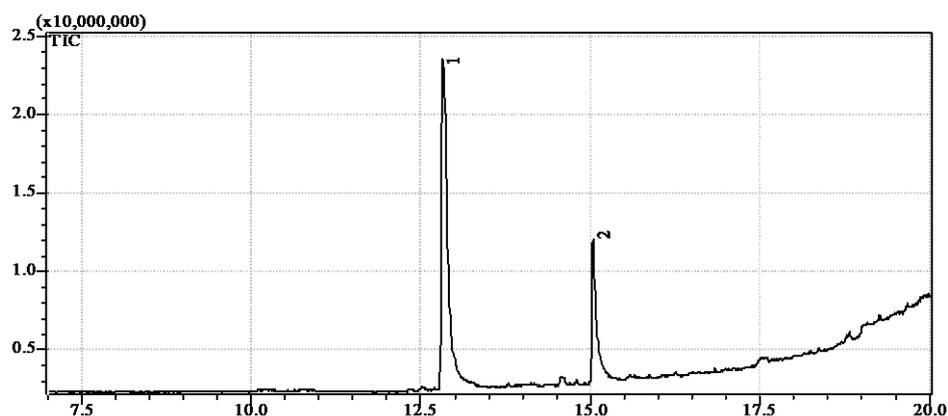


Figure 4.43: TIC obtained by Py-GC-MS of gradient fraction 1 of MBC LP 127

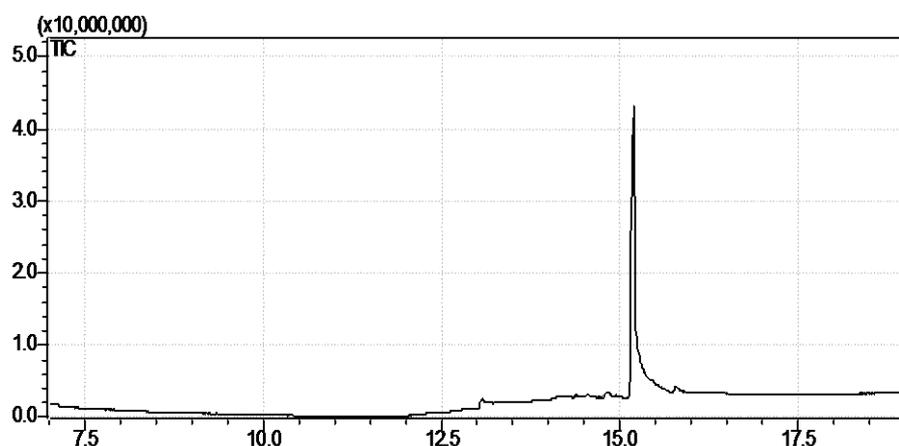


Figure 4.44: TIC obtained by Py-GC-MS of gradient fraction 2 of MBC LP 127

In Fig. 4.43 two peaks are observed around 13 and 15 min retention time for the first fraction of the gradient separation. Based on the retention times and the resulting mass spectra these peaks were identified as p-dioxanone and ϵ -caprolactone respectively.

Fig. 4.44 shows the TIC of the second fraction from gradient chromatography. Contrary to fraction 1, the second fraction of the gradient separation shows only one peak at 15 min retention time. This peak is identified on the basis of the retention time and mass spectra as ϵ -caprolactone.

As illustrated in Fig. 4.24, gradient chromatography of the MBCs shows two peaks that are clearly separated. The first peak eluting at 3 min retention time should contain only very little PPDO. The second peak which elutes with the gradient in the range of 6-8 min retention time is expected to contain a high portion of PCL. During the identification process by means of FTIR, no PCL was identified in the first peak and no PPDO was identified in the second peak. As a consequence, these results stand in contradiction with Py-GC-MS where the TIC of the first fraction shows both PPDO and PCL and the TIC of the fraction 2 shows only PCL.

While FTIR investigations of the chromatographic fractions of the gradient chromatography identified peak 1 as being composed of PPDO, while peak 2 consists of PCL only, pyrolysis-GC-MS studies of the fractions 1 and 2 in the gradient chromatograms of the MBCs revealed that fraction 1 contains both PCL and PPDO in different amounts, and fraction 2 contains only PCL. In order to get quantitative information on the composition of the both peaks from gradient chromatography, Py-GC-MS was used.

Since here the task was to determine the PPDO composition in fraction 1 and 2 of the gradient chromatography. The construction of the calibration curve was made in a similar way as in the previous section. The only difference here is that the calibration was plotted with PPDO area as a function of weight percentage (wt%) of PPDO as illustrated in Fig. 4.45. As expected for pyrolysis GC-MS, the calibration curve is non-linear which means that the response factor is different for both polymers in pyrolysis GC-MS. The third degree polynomial function was used for fitting the curve.

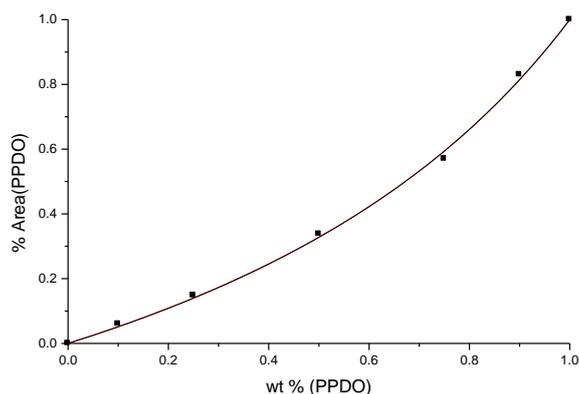


Figure 4.45: Calibration curve for relation between PPDO composition and peak area of PPDO

In order to determine the PPDO compositions for fractions 1 and 2 of the MBCs from gradient chromatography of the samples were manually fractionated in analytical scale. Each fraction was separately pyrolyzed by injecting the solution. An example of the TIC of fractions 1 and 2 of MBC LP 127 has been given in Figs. 4.43 and 4.44. By using the calibration curve in Fig. 4.45 the compositions of PPDO in fractions 1 and 2 of the MBCs was determined. The results are summarized in Table 4.8.

Table 4.8: PPDO content (wt%) in fraction 1 and 2 of MBCs as determined by pyrolysis GC-MS.

Sample	Fraction 1 PPDO-content (wt%)	Fraction 2 PPDO- content (wt%)
LP 126	88	10
LP 127	85	9
LP 099	97	0

Based on quantitative studies in Table 4.8, the first peak of the gradient chromatography of the MBCs showed more than 80 % (wt%) of PPDO content. This indicates that the peak 1 of the gradient chromatography of the MBCs consists largely on PPDO-units and a small content of PCL-units (Table 4.8). In the second peak of the gradient chromatography of the MBCs, 0-10% (wt%) of PPDO content

was found. This implies that the peak 2 of the gradient chromatography of the MBCs is principally made of PCL-units. Thus, the absence of the p-dioxanone peak in the TIC of the fraction 2 (Fig. 4.44) might be due to the sensitivity of the system.

Please note that fractions 1 and 2 from gradient chromatography for other MBCs samples gave the similar results in terms of identification of composition of each peak.

The results above are in an agreement with the interpretation of the retention times in gradient chromatography, where it was concluded that fractions 1 and 2 of the MBCs from gradient chromatography are composed mainly of PPDO and PCL, respectively.

Since the two previous methods FTIR and pyrolysis-GC-MS have shown different results on identification of the gradient chromatography peaks, but have produced meaningful result on the composition of the components, in order to gain more information on the nature of gradient chromatography peaks and on their composition on-line coupling of gradient chromatography and proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy ($^1\text{H-NMR}$) was used.

4.5.4 On-line coupling of gradient chromatography and $^1\text{H-NMR}$

For supporting the information obtained above, the samples of the MBC were also examined by direct coupling of gradient HPLC and proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy. This method will minimize all problems of degradation and contamination and should allow a direct analysis of different peaks. On-line $^1\text{H-NMR}$ experiments were performed using solvent suppression techniques. As an example for on-line coupling of gradient chromatography and $^1\text{H-NMR}$, the NMR-spectra at different retention times of MBC LP 127 in gradient chromatography are illustrated in Fig. 4.46.

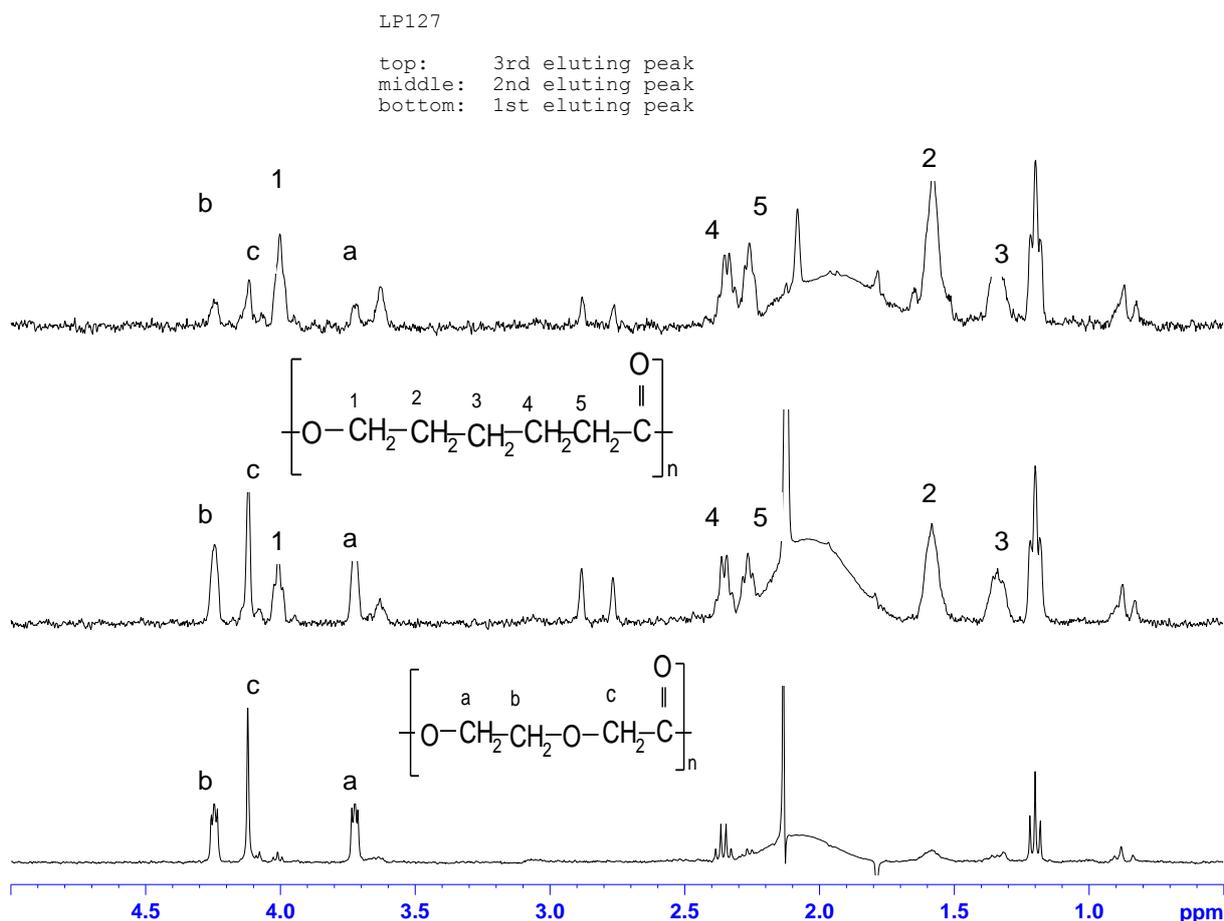


Figure 4.46: $^1\text{H-NMR}$ spectra of MBC LP 127 at different retention time of peak 1 and peak 2 of the gradient chromatography. From bottom to the top increasing retention time

Fig. 4.46 represents $^1\text{H-NMR}$ spectra of MBC LP 127 at different retention time of peak 1 and peak 2 of the gradient chromatography. The bottom spectrum corresponds to the elution of peak 1 at 3 min (Fig.4.24) from gradient chromatography. The middle and the upper spectra correspond to the middle and the last part of peak 2 which elutes between 6-8min (Fig. 4.24).

In the spectrum of the first peak, the first triplet at 4.25 ppm belongs to the hydrogen attached to carbon labeled b, and the second triplet at 3.7 ppm corresponds to the hydrogen attached to carbon labeled a. The hydrogen attached to the carbon labeled c represents the singlet at 4.15 ppm. The NMR-spectrum of the first peak of gradient chromatography therefore is consistent with the spectrum of PPDO. On the basis of this spectrum it is to be accepted that the first peak of gradient chromatography consists mainly of PPDO. Smaller resonances are observed at 4 - 4.1 ppm and at 1.3

– 1.7 ppm which cannot be assigned to those of PPDO and are suspected to be impurity.

The middle spectrum was taken in the middle part of peak 2 of MBC LP 127 from gradient chromatography. This spectrum shows five additional resonances as compared to the main resonances of the lowest spectrum in Fig. 4.46. These five additional resonances at 4, 2.3, 2.2, 1.6 and 1.3 ppm can be assigned to the hydrogens attached to the carbons labeled 1, 4, 5, 2, and 3 of PCL, respectively. The middle spectrum however shows comparable signal intensities of both components PPDO and PCL. The presence of PPDO and PCL peaks in the middle spectrum proved that in the middle part of peak 2 both components PPDO and PCL eluted simultaneously.

The upper spectrum corresponds to the end part of peak 2 of MBC LP 127 from the gradient chromatography. The results are typically identical to those of the middle part of peak 2. But here, the relative intensity of the PPDO signals indicated by the letters a, b and c is considerably lower than the intensity of PCL resonances. Accordingly, it is clear that at the end of peak 2 of MBC LP 127 from gradient chromatography both components PPDO and PCL are also present with a large content of PCL since the intensities of PPDO peaks are weaker. Note that the results commented above could also be verified for other MBC samples.

From on-line coupling gradient chromatography and ^1H - NMR results the following conclusion can be draw:

- On-line coupling of gradient chromatography and ^1H -NMR has also verified the pyrolysis-GC-MS results by showing that peak 1 (lower spectrum) of MBC LP 127 from gradient chromatography contains only PPDO, while the peak 2 (middle and upper spectra) contains both PPDO and PCL peaks. The presence of PPDO peaks in peak 2 of the gradient chromatography let's to the assumption that the peak 2 of gradient chromatography is made of PCL-MBP and/or block copolymers (PPDO-PCL-MBC). The difference in peak intensity between the middle and upper spectra is due to a chemical composition distribution of the MBCs.

In order to determine PPDO content in different MBCs, first the $^1\text{H-NMR}$ spectrum of the MBCs needs to be recorded. Fig. 4.47 shows an example of $^1\text{H-NMR}$ spectrum of MBC LP 099.

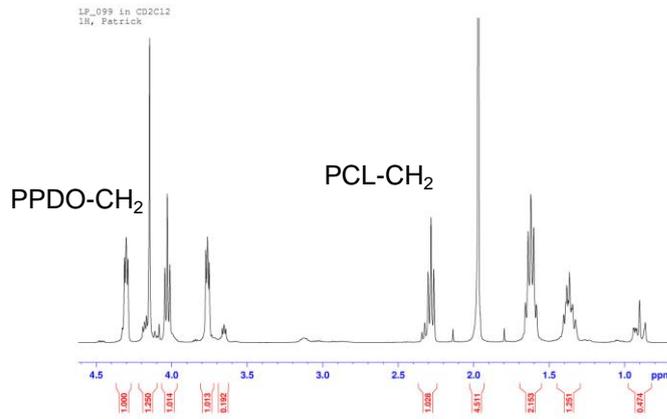


Figure 4.47: $^1\text{H-NMR}$ spectrum of MBC LP 099

As a typical example for the $^1\text{H-NMR}$ spectrum of a MBC, Fig. 4.47 shows the spectrum of MBC LP 099. In order to determine PPDO content in MBC LP 099, the signal at 4.30 ppm from PPDO and the signal at 2.28 ppm from PCL were used. The PPDO content was determined by using equation. 4.3.

$$\begin{aligned}
 \text{Weighpercent}(PPDO)\% &= \frac{m_{PDO}}{m_{PDO} + m_{CL}} * 100 \\
 &= \frac{n_{PDO} * M_{PDO}}{n_{PDO} * M_{PDO} + n_{CL} * M_{CL}} * 100 \\
 &= \frac{\frac{I_{PDO}}{N_{PDO}} * M_{PDO}}{\frac{I_{PDO}}{N_{PDO}} * M_{PDO} + \frac{I_{CL}}{N_{CL}} * M_{CL}} * 100
 \end{aligned} \tag{4.3}$$

where, I_{PDO} : integral intensity of CH_2 - PPDO at 4,30 ppm,; N_{PDO} number of protons of CH_2 -PPDO at 4,30 ppm, m_{PDO} : mass of repeating unit of PPDO,;

I_{CL} integral intensity of CH₂-PCL at 2,28 ppm , N_{CL} : number of protons of CH₂-PCL at 2,28 ppm and m_{CL} : mass of repeating unit of PCL

In Table 4.9, PPDO contents of different MBCs measured by ¹H-NMR are compared with the PCL contents of the MBCs from synthesis. This comparison is graphically represented in Fig. 4.48 as well.

Table 4.9: Comparison of PPDO contents of the MBCs measured by ¹H NMR with those from synthesis

Samples	PPDO content measured by ¹ H-NMR (wt%)	PPDO content from synthesis (wt%)
LP 099	54	50
LP 101	51	50
LP 102	49	50
LP 103	45	50
LP 166	47	50
LP 126	49	60
LP 127	54	60

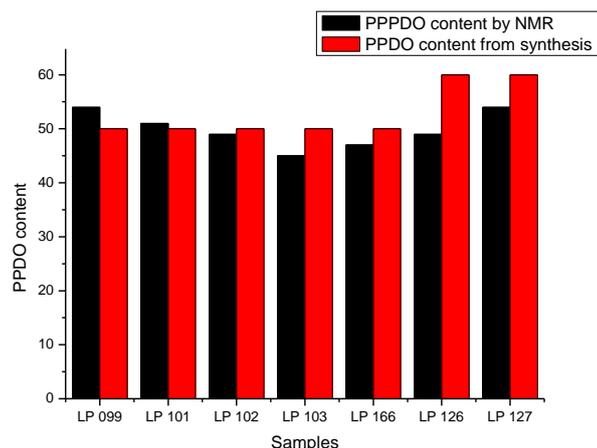


Figure 4.48: Graphic comparison between the PPDO contents of the MBCs measured by ^1H NMR with the ones from synthesis

Table 4.9 and Fig. 4.48 show the comparison between the PPDO contents of different MBCs measured by ^1H -NMR and the PPDO contents of the MBCs from synthesis. One can see that the values obtained by ^1H -NMR good agreement the data obtained from synthesis. These results also matches with the results obtained by means of LC-FTIR and Py-GC-MS (from pyrolysis results one exception was found for MBC LP 127 where a deviation of 20% is observed. (See page 76).

In order to further support the result on the composition of the both peaks of the gradient chromatography the samples were fractionated several times in fraction 1 and 2. The solvent was evaporated and the ^1H -NMR-spectra were acquired. An example of ^1H -NMR spectrum of fraction 1 of MBC LP 101 is illustrated in Fig. 4.49.

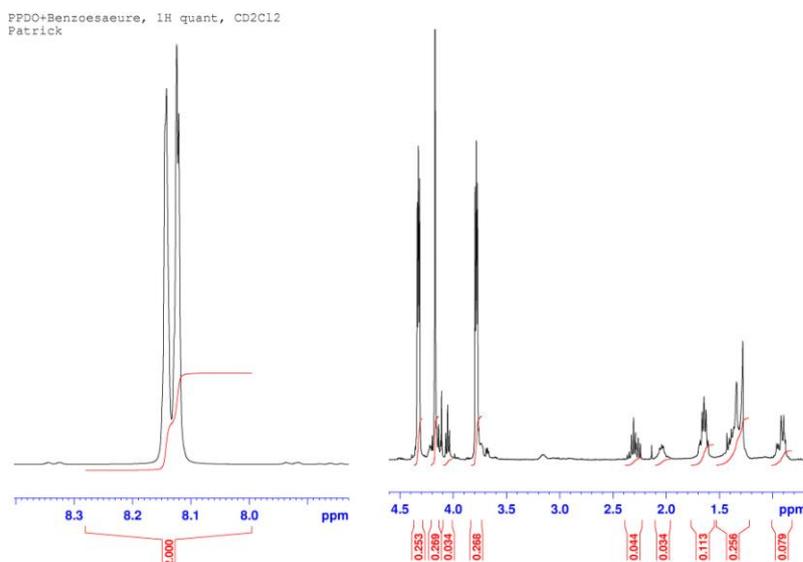


Figure 4.49: Example of

¹H-NMR spectrum of fraction 1 of MBC LP 101 with benzoic acid as reference.

Fig. 4. 49 shows an example of ¹H-NMR spectrum of fraction 1 of MBC LP 101. The ¹H-NMR spectra of the peaks 1 and 2 of the gradient chromatography of the MBC LP 101 confirm the presence of both PPDO and PCL. Characteristic signals found at 1.3, 1.6 and 2.3 ppm are attributed to PCL, and the signals at 3.5 and 4.5 ppm are assigned to the PPDO. The signals at 8.1-8.2 ppm belong to the reference benzoic acid. Other signals at 0.9 and 2.0 ppm might be due to impurity. In order to calculate the composition of PPDO in peak 1 and 2 of the gradient chromatography of the MBCs, the absolute masses need to be determined. Peak 1 and 2 of the gradient chromatography of the MBCs need to be fractionated. Knowing that manual fractionation is time consuming we limited the investigation to two MBCs: MBC LP 101 and LP 102. For the fractions 1 and 2 of the MBC LP 101 for example, the total mass of the fraction 1 and 2 were 2,28 mg and 2,83 mg, respectively. By using benzoic acid as an internal standard of known mass and purity, the absolute masses of PPDO and PCL were determined in each fraction. The absolute masses of PPDO in fraction 1 and 2 were 1,35 mg and 0,42 mg while for PCL were 0,33 mg and 1,63 mg, respectively. The remaining mass of 0,5 mg in fraction 1 and 0,78 mg in fraction 2 might be due to impurity. Similarly, in MBC LP 102, the absolute masses of PPDO in fraction 1 and 2 were 1,45 mg and 0,42 mg while for PCL 0,33 mg and 1,63 mg,

respectively. By using the formula 4.3, the compositions of PPDO in fraction 1 and 2 were determined. The obtained results are summarized in Table 4.10.

Table 4.10: PPDO contents in fractions 1 and 2 of the MBCs determined by $^1\text{H-NMR}$

Samples	Fraction 1 PPDO content (wt%)	Fraction 2 PPDO content (wt%)
LP 101	81	20
LP 102	87	14

The quantitative studies conducted on the fractions 1 and 2 of the gradient chromatography of the MBCs in Table 4.10 shows that the fraction 1 contains more than 80 % (wt%) of PPDO. This indicates that the peak 1 of the gradient chromatography of the MBCs consists mostly of PPDO-units and small content of PCL-units (Table 4.10). However, the fraction 2 of the gradient chromatography of the MBCs contains 14-20% (wt%) of PPDO. This suggests that the peak 2 of the gradient chromatography of the MBCs is principally made of PCL-units. The absence of PCL in $^1\text{H-NMR}$ spectrum of fraction 1 might be due to the sensitivity of the coupling gradient chromatography and $^1\text{H-NMR}$ system.

The quantitative results on $^1\text{H-NMR}$ are in an agreement with Py-GC-MS results. They showed that the peak 1 of the gradient chromatography of the MBCs is predominantly composed of PPDO-units, while the peak 2 of the gradient chromatography of the MBCs consists mainly of PCL-units.

4.6 Summary: comparison of the PCL contents measured by $^1\text{H-NMR}$, pyrolysis GC-MS, SEC-FTIR spray device and PCL contents according to synthesis

In order to get a better view on the reliability of the methods used to determine the compositions of the MBCs a comparison of the results obtained by $^1\text{H-NMR}$, pyrolysis GC-MS and LC-FTIR on PCL was made. The results are compared in Table 4.11 with the data expected from synthesis. Additionally a graphical comparison is made in Fig. 4.50

Table 4.11: Comparison of PCL contents of the MBCs measured $^1\text{H-NMR}$, pyrolysis GC-MS, LC-FTIR and PCL contents of the MBCs from synthesis

Samples	$^1\text{H NMR}$ (wt%)	Pyrolysis (wt%)	SEC-FTIR (wt%)	Synthesis (wt%)
LP 099	51	49	43	50
LP 101	52	45	50	50
LP 102	51	52	48	50
LP103	57	53	44	50
LP 166	45	56	52	50
LP 126	51	48	33	40
LP 127	48	60	38	40

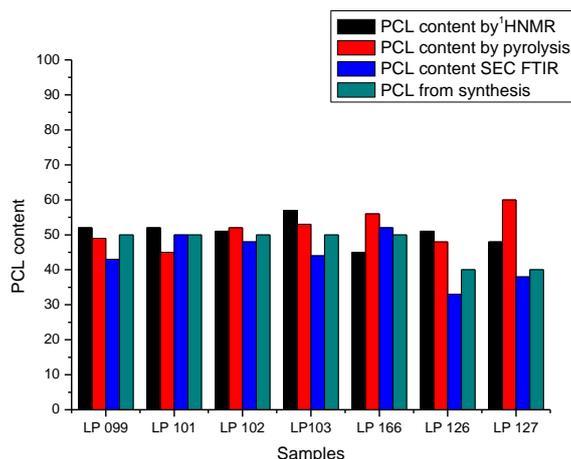


Figure 4.50: Graphic comparison between the compositions determined by ¹H NMR, pyrolysis-GC-MS, SEC-FTIR with the expected values from synthesis.

PCL contents of all MBCs as determined by ¹H-NMR, Py-GC-MS and SEC-FTIR is in meaningful agreement with the PCL-contents of the MBCs from synthesis. One exception is MBC LP 127 where the PCL content measured by pyrolysis GC-MS deviates by 20% from the expected value. Since the PCL contents for other MBCs measured by Py-GC-MS matched more or less with PCL contents from synthesis, the deviation of MBC LP 127 let's to the assumption that the composition from the synthesis as given by the supplier might be incorrect.

The results on the compositions of the gradient chromatographic fractions 1 and 2 determined by LC-FTIR, Py-GC-MS and ¹H NMR have shown good agreement. They have showed that the fraction 1 of the gradient chromatography is principally made of PPDO-units while the fraction 2 is mostly made of PCL-units.

From the above results it can be concluded that ¹H-NMR, SEC-FTIR as well as Py-GC-MS allow reasonable quantification of the contents of the MBCs under investigation. The MBCs under investigation are very heterogeneous.

The results obtained throughout this investigation were valuable since they have led to further optimization of the synthesis procedure by the project partner. The unexpected broad heterogeneity of the MBCs samples might influence the properties of the polymers. In addition it complicated establishing structure-property relations.

Therefore, optimizations of the synthesis process were performed by the project partner. One is a more elaborated process (two-step growth polymerization) which yielded MBCs LP 151, 177, 185 187 and 188. In the two-step growth polymerization, the first step is to react the first polyol with an excess of the diisocyanate to form a diisocyanate terminated oligomer. The second step consists of adding the second polydiol in order to convert the isocyanate-terminated prepolymer to the final polyurethane. This procedure was expected to produce more homogeneous MBCs. Another procedure is a one-step growth polymerization with different solvents (modified synthesis) which yielded the MBCs AMC 9, 27, 22/3, 34 and 52. By changing the solvent one might avoid early phase separation which is suspected to be one cause of the heterogeneity of MBC.

The relevant characteristic information on molecular parameters of different samples given by the supplier is listed in Table 4.12.

Table 4.12: Molecular parameters of different the MBCs from the modified synthesis and the two step polymerization as given by supplier

Samples ID	Abbreviation	M_w ($\text{g}\cdot\text{mol}^{-1}$)	M_n ($\text{g}\cdot\text{mol}^{-1}$)	PDI	Composition wt%(PPDO/PCL)
PPDO-20+22 /PCL2k	LP151	337000	38000	8,8	50/50
PPDO-34 /PCL2k	LP177	365000	50000	7,3	50/50
PPDO-37 /PCL2k	LP185	595000	41000	14,5	50/50
PPDO-37 /PCL2k	LP187	425000	43000	9,8	50/50
PPDO-37 /PCL2k	LP188	327000	36000	9,0	50/50
PCL*3-bl-PPDO-7 (PCL-10k-NCO 9)	MBC-9	-	-	-	50/50
PPDO*bl-PCL-10k (PPDO-7-NCO 2)	MBC-22/3	-	-	-	50/50
PCL*3-bl-PPDO-7 (PCL-10k-NCO 17)	MBC-27	-	-	-	50/50
PCL*4-bl-PPDO-7 (PCL-2k-NCO 19)	MBC-34	-	-	-	50/50
PPDO*bl-PCL-10k (PPDO-7-NCO 5/6d)	MBC-52	-	-	-	50/50

Table 4.12 shows molecular parameters of different MBCs from the modified synthesis and the two step polymerization as given by supplier. This result is difficult to be interpreted since no further information on the characterization of these samples was given by manufacturer. By comparing the M_w and M_n of the MBCs from the two step polymerization in Table 4.12 with those of the original synthesis in Table 4.1 as given by supplier, one can see that the two step polymerization as produced the MBCs with large value of M_w and M_n than those of original samples. This might be due to the different reactivities between the two polymerization reactions. In addition, the PDIs of the MBCs from the two step polymerization are very large. It can be hypothesized that the molar mass distribution was multimodal this might indicate that residual diols are present in the MBCs samples.

The MBCs synthesized by these procedures were investigated under the same gradient chromatography conditions as defined before.

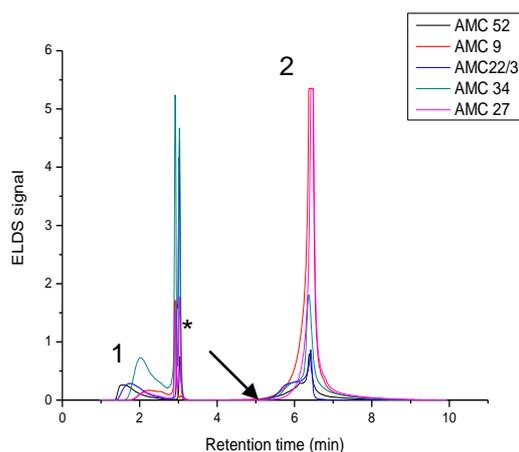


Figure 4.51: Chromatograms of gradient chromatography of the multiblock copolymers from modified synthesis (MBC AMC 9, 27, 22/3, 34 and 52), mobile phase: ACN-DCM, (Nucleosil-C₁₈, particle size 5 μ m, and pore diameter 100 Å , column dimension 250 mm \times 4.0 mm), gradient: ACN-DCM linear at 10min, flow-rate: 1.0mL/min, Detector: evaporative light-scattering (ELSD)

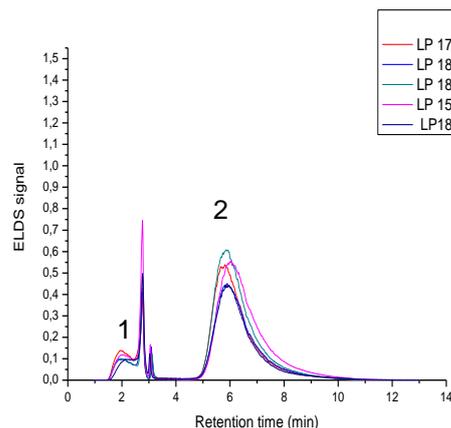


Figure 4.52: Chromatograms of gradient chromatography of the multiblock copolymers from two step polymerization (MBC LP 151, 177, 185 187 and 188), mobile phase: ACN-DCM, (Nucleosil-C₁₈, particle size 5 μ m, and pore diameter 100 Å , column dimension 250 mm \times 4.0 mm), gradient: ACN-DCM linear at 10min, flow-rate: 1.0mL/min, Detector: evaporative light-scattering (ELSD)

Figs. 4.51 and 4.52 show the chromatograms from gradient chromatography of the MBCs from the modified synthesis (Fig. 4.51) and from the two step polymerization (Fig. 4.52). In both figures two main peaks 1 and 2 are observed. Based on retention times peak 1 is assigned to be PPDO/PPDO-MBP and peak 2 to PCL/PCL-MBP. Based only on the retention time of peaks without any further characterization, it is difficult to say whether the news MBC synthesized have the same compositions as the previous MBCs or not. In order to investigate whether the changes made in the synthesis procedure have finally resulted in more homogenous samples or not, the relative peak areas of gradient chromatography were compared in terms of percentage peak 1/peak 2 of different MBCs. Since previous results have proven that peak 1 and peak 2 are composed principally of PPDO and PCL, the measure of the relative peak areas might be referred to as heterogeneity of the samples. Fig. 4.53 shows the so obtained relative peak areas for the samples prepared by the different synthetic procedures.

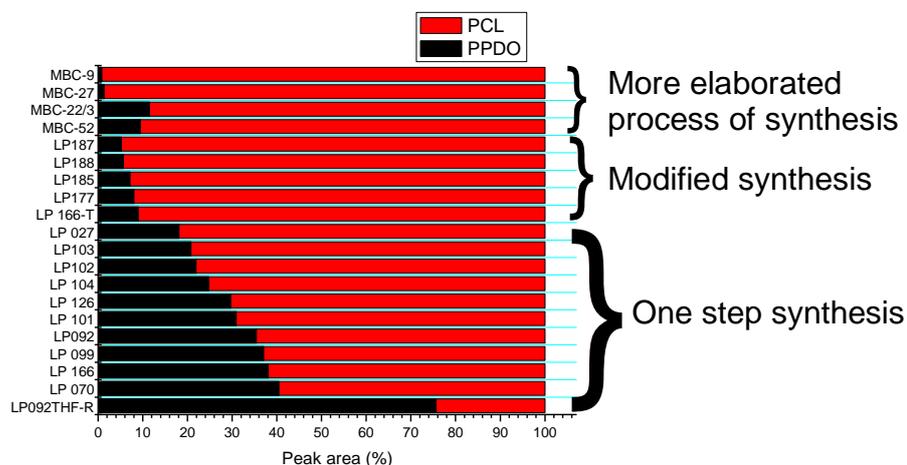


Figure 4.53: Relative peak areas of different multiblock copolymers

In the lower part of the figure, the samples produced by the original one-step process are shown. The middle part is describing samples made by the modified synthesis and the upper part shows the samples produced with more elaborated two-step process. The black bars represent the relative peak area of the components eluted within the range of pure PPDO and can be used as the first estimation for the homogeneity of the samples. The red bars indicate the relative peak areas of the eluting PCL-rich peaks in gradient chromatography. This peak might contain with the block copolymers since the block copolymers with comparable portions of the two diols components should elute in gradient in the similar retention behavior as pure PCL. One can see that samples synthesized by the more elaborated process show significant smaller fractions of the first eluting peak, indicating that lower amounts of the high PPDO-containing products are formed by these synthetic strategies. This indicates that the samples produced with these two methods are more homogeneous than those synthesized by the original process. One hypothesis to explain the unexpected high heterogeneity of the samples produced by the original method might be that both polyols used during the polymerization have different reactivities. On the other hand, both the PPDO- and the PCL-diols have the same end groups. Another reason might be an incompatibility of the reactants. Thus the solvent might not effectively bring them into one phase. This might result in a phase separation into a PPDO-rich and a PPDO-poor but PCL-rich phase during the polymerization. The

simultaneous copolymerization in two phases of different composition might then result in a high heterogeneity of the final product. This assumption could also explain the observed more homogenous product distributions when changing the reaction solvent.

5. Experimental Part

5.1 Chromatographic equipment

Separations were carried out on a Shimadzu system (Kyoto, Japan) comprising a DG-2410 degasser, a FCV-10ALvp solvent mixing chamber, a LC-10ADvp pump. The temperature was regulated with a column oven model K4 from Techlab. For detection, an evaporative light scattering detector, ELSD 1000 (Polymer Laboratories, Church Stretton, England) and/or a differential refractive index detector Waters 450 (Waters, Milford, MA, USA) was used. For data collection and processing the software package "WinGPC-Unity" software v. 7.0" (Polymer Standards Service GmbH, Mainz, Germany) was used.

5.2 Chromatographic columns

- **SEC**

A set of two of PSS SDV columns (10^3 , 10^5 Å, each 300 x 8 mm I.D.; Polymer Standards Service, Mainz, Germany) was used.

- **Gradient HPLC and LCCC**

Nucleosil C18; (Macherey–Nagel, Düren, Germany). Particle size 5 µm, pore diameter 300 Å, column dimensions 250×4.0 mm i.d.

Nucleosil bare silica (Macherey–Nagel, Düren, Germany). Particle size 7 µm, pore diameter 1000 Å, column dimensions 250×4.0 mm i.d.

Gradient HPLC and LC-CC samples were prepared by dissolution of samples in highly concentrated HFIP (3-5 drops), followed by dilution with ACN.

Following solvents were used as received:

Acetonitril (ACN), HPLC grade, Acros Organics, Dichloromethane (DCM), Chloroform (CHCl_3) and Dimethylformamide (DMF), were purchased from VWR (West Chester, PA, USA) and are all HPLC grade.

Tetrahydrofuran (THF, BASF) was refluxed and distilled from CaH_2

- **Polymer standards**

All narrow distributed polymer standards of polystyrene (PS) are synthesized and distributed by Polymer Standards Service GmbH (Mainz, Germany), unless otherwise mentioned.

- **Samples**

Samples were delivered by GKSS Forschungszentrum Geesthacht GmbH, (Germany, Teltow):

- **Molar mass analysis by MALDI-ToF-MS**

Mass spectra were acquired using an AXIMA ToF² Spectrometer (Shimadzu Biotech, Kyoto, Japan). Spectra were recorded and integrated with the software Shimadzu Biotech. The polymers were dissolved in HFIP at a concentration of 0.5-4 mg/mL. The matrix (trihydroxyanthracene) was dissolved in dioxane at a concentration of 10mg/mL.

- **LC-FTIR interface and FTIR spectrometer**

LC-FTIR coupling accomplished using a LC-Transform 600XY system (LabConnections, ^A mocon company, Northborough, MA, USA). After evaporation of the mobile phase samples were deposited on square Germanium plates (55 x 55 mm). Spraying conditions were: gas flow 30 psi, the nozzle temperature 160°C, plate speed of 20 mm/min.

FTIR analyses of the fractions were carried out on a Nicolet Protégé 460 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA). Spectra were recorded between 800 and 4000 cm^{-1} every 2 mm along the sample track. 32 scans were taken per spectrum. Data acquisition and treatment were performed with the software Omnic developed by the spectrometer manufacturer:

- **NMR**

NMR spectra were acquired on a 400 MHz spectrometer Varian (Mercury VX 400, Sao Paulo, USA) with a 5 mm, inverse detection CID probe at an observing frequency of 400.12 for ^1H . Samples were dissolved in deuterated (CD_2Cl_2) Further experimental parameters were as follows:

- ✓ ^1H -NMR: 90° exciting pulse 9.8 μs , 64k data points corresponding to an acquisition time of 7s, relaxation delay of 30s and total of 128 scans and spectra width was 12 ppm.
- ✓ LC-NMR: measurements were performed using a probe containing a 60 μL flow cell. The 90° ^1H pulse was 4.7 μs , 16k data points corresponding to an acquisition time of 1.0s, relaxation delay of 0.1 s and total of 16 scans. Spectra width was 20ppm and WET with ^{13}C decoupling was optimized to suppress signals of chloroform.

- **Pyrolysis-GC-MS**

The analysis of the pyrolysis products was carried out using the SHIMADZU QP-5000 GC/MS system (Analytical Instrument Division, Kyoto, Japan). Pyrolyzer: Pyr 4A, Pyrolyzation temperature: 450°C , column: RTX-5Sil MS, 30m, 0,25mm, 5 μm , Gas: He, Gas flow: 7,1mL/min, Temperature program: $60\text{-}320^\circ\text{C}$, Scanning range: 33-200m/z, Data point density: 0,5sec, Sample amount: 20 μL .

5.3 Polymer synthesis

The following part of the thesis gives a short overview on the synthetic routes of the macrodiols, multiblock polymers and multiblock copolymers used throughout the present work. Multiblock polymers are defined as polymers which are linked with two or more macrodiols of the same type, multiblock copolymers however are defined as polymers which are linked with two or more macrodiols of the different type.

- **Synthesis of macrodiol**

The macrodiols used for the synthesis of the multiblock polymers (MBP) are *p*-dioxanone (PPDO) and ϵ -caprolactone (PCL) diols. PCL-diols are commercially available, while PPDO-diols are not. Thus, the PPDO-diols were synthesized by ring opening polymerization from commercially available *p*-dioxanone (PDO) with a diol as initiator [92-98]. Fig. 5.1 illustrates the synthesis of PPDO-diols.

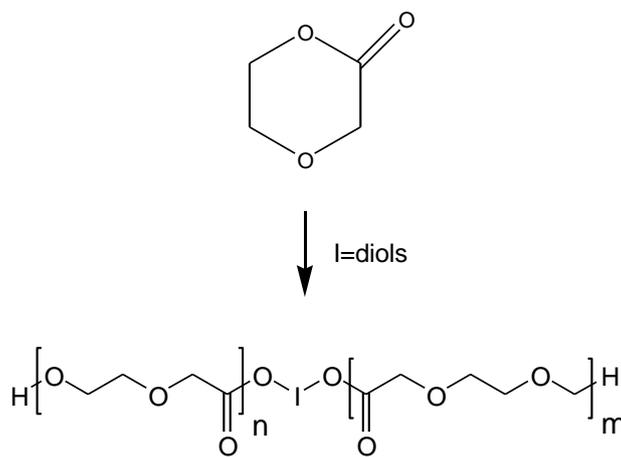


Figure 5.1: Synthesis of poly (*p*-dioxanone) diol (PPDO) from *p*-dioxanone, I=initiator

- **Synthesis of the multiblockpolymers (MPB)**

The multiblock polymers (MBP) of PPDO and PCL were synthesized by reacting the respective macrodiol (PPDO- or PCL-diols) with TMDI in solution at elevated temperature. Fig. 5.2 shows a schematic representation of the synthesis of the multiblockpolymers.

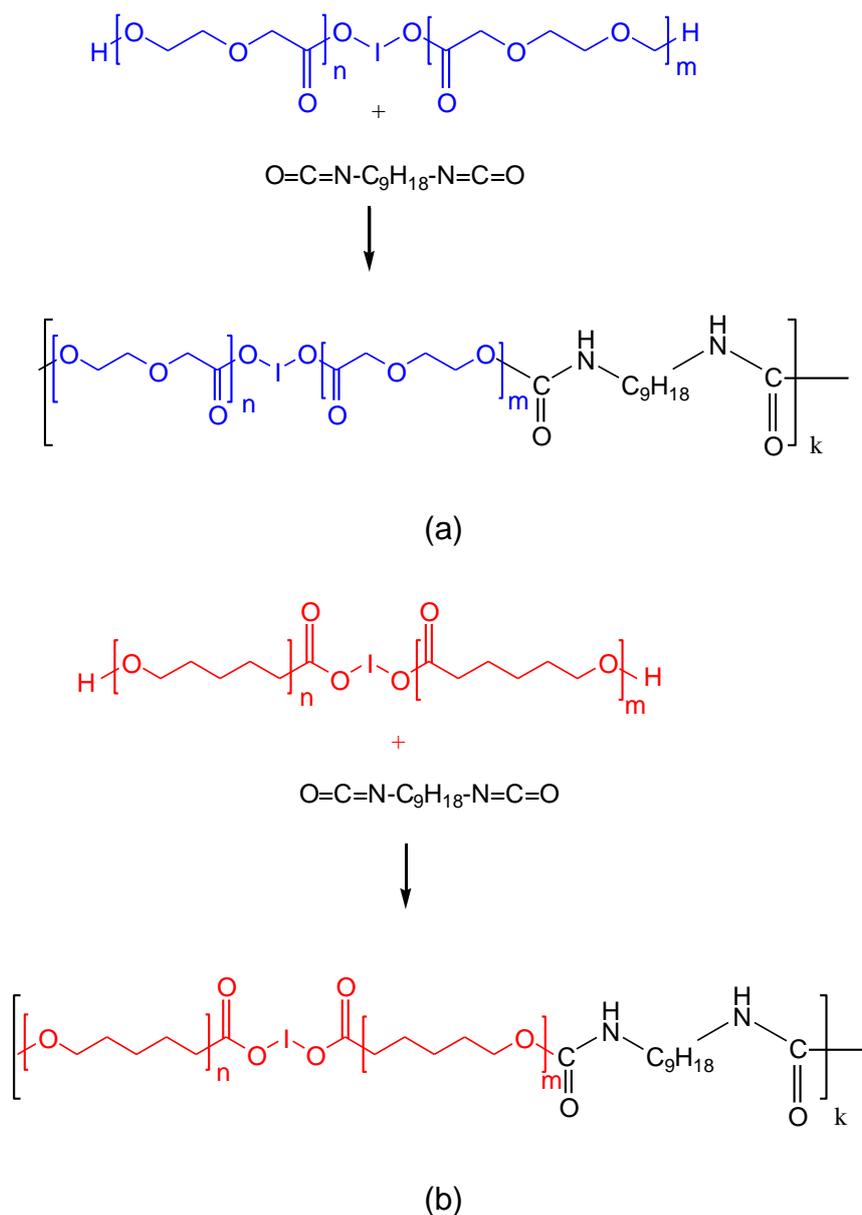


Figure 5.2: Schematic representation of the synthesis of multiblock polymers: (a) PPDO-MBP and (b) PCL-MBP

- **Synthetic methods of polyurethane by step growth**

The various methods for synthesizing polyurethanes can be differentiated according to the medium of preparation (bulk, solution, water) and according to the addition sequence of the reactants (one-step process, prepolymer process). In some cases, catalysts are added to accelerate the polyaddition reaction [12]. Bulk polymerization,

either one-step or two-step, has been the main industrial process for polyurethane production, because of its environmentally friendly solvent-free synthesis. Solution polymerization has largely been used in laboratory synthesis of polyurethanes. The different synthetic processes have an effect on the heterogeneity of the final product. For example, during polyurethane bulk synthesis, the incompatibility between the reactants might induce formation of a heterogeneous system or the system becomes heterogeneous at a relatively early stage of the polymerization. This might lead to formation of the heterogeneous polymer in both molar mass and chemical composition. This heterogeneity might affect the properties of the final product. However, in the solution process, the problem of heterogeneity can be avoided by selection of a suitable choice of solvent. Reactants incompatible in bulk might be dissolved in a suitable solvent resulting in a homogenous one phase system. Common solvents used in polyurethane synthesis are dipolar aprotic solvents including N, N'-dimethylacetamide (DMAc) and dimethylformamide (DMF). In a one step synthesis, the reaction is carried out by simultaneously mixing a polyol, and diisocyanate together in the reaction solvent and heating the solution at elevated temperature. In some cases, catalysts are applied to accelerate the reaction. The reaction rate is usually determined by the temperature profile of chemical reaction [13].

- **Synthesis of the investigated multiblock copolymers (MBCs)**

The MBC used in this study were synthesized as one-step reaction by simultaneously mixing the macrodiols (PPDO- and PCL-diols), and trimethyl hexamethylene diisocyanate (TMDI), together in the solvent and heating the solution at elevated temperature. Fig. 5.3 shows a schematic representation of the synthesis of the multiblock copolymers.

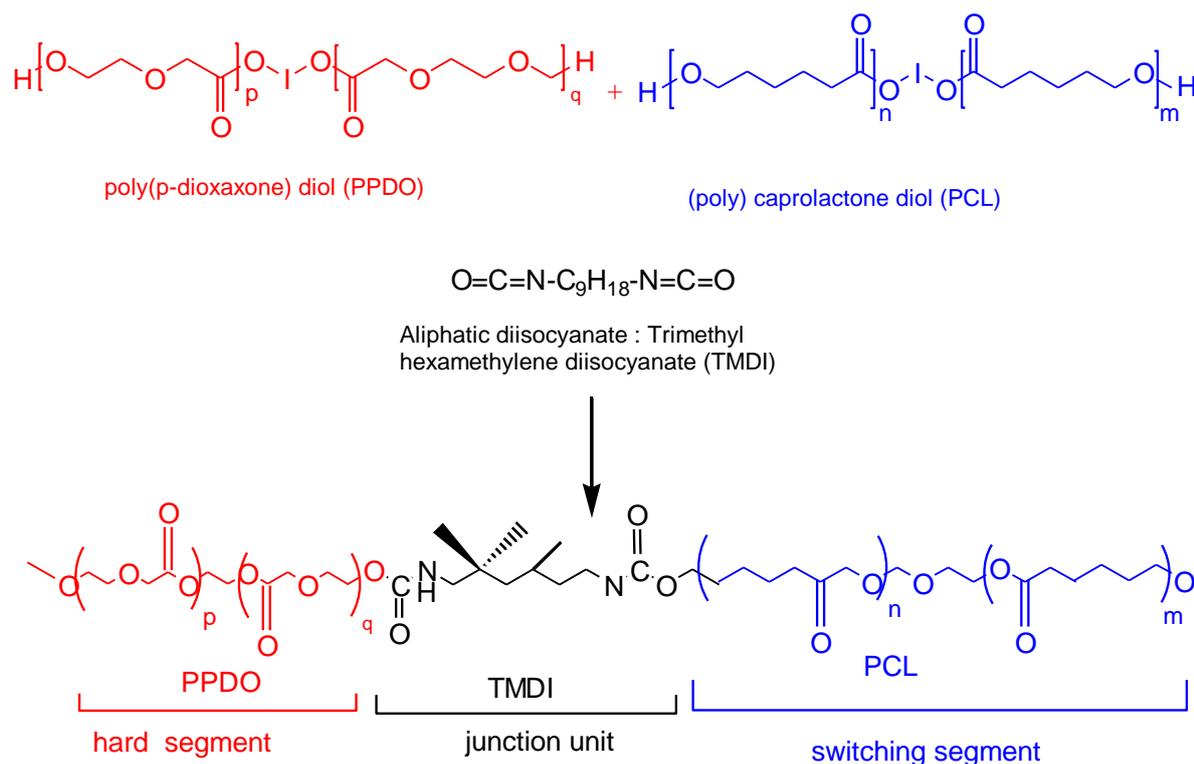


Figure 5.3: Schematic representation of the synthesis of multiblock copolymers (MBC)

The simultaneous reaction of PPDO-diols, PCL-diols and TMDI might result in MBC formation. However, due to the statistical processes inherent in any polymerization process the products might be heterogeneous in both molar mass and chemical composition. This heterogeneity might also affect the properties of the final polymer.

6. Summary and Conclusions

The interest and the need for innovative products with new properties lead to the development of a large variety of new complex polymer materials. This results in an increasing demand in characterization tools allowing understanding the molecular structure of these new products in order to relate them to the observed properties, which finally will allow establishing structure-property relationships. Such knowledge allows for optimization of the synthesis parameters and consequently of the final application properties.

The aim of this work was to develop analytical methods and tools to characterise the functionality type distribution (FTD) of poly (p-dioxanone)- (PPDO) and poly (caprolactone)-diol (PCL) samples. In addition information on the heterogeneities of multiblock copolymers (MBC) derived by reacting mixtures of the two polymeric diols with diisocyanates was requested.

First chromatographic conditions were developed to determine the number of OH end groups in PCL and PPDO-diols. Critical conditions for PCL were established on a polar stationary phase, using 92%/8% dichloromethane (DCM) and tetrahydrofuran (THF). For all the PCL-diols two peaks were observed. The first peak eluted close to the void volume of the column indicating the presence of PCL molecules without polar OH end groups. The second peak eluted at higher retention times. This is due to the additional interaction of the two OH end group with the stationary phase. Although critical conditions were applied, the PCL-diols eluted in the order of decreasing molar mass. The reason for this elution behaviour might be that only at high molar masses of the two OH end groups adsorb statistically independent. If the polymer chain, however, is short, the statistical independence is not valid any longer. If the first OH-group is adsorbed, the second OH-group is in the proximity of the stationary phase and the probability for its simultaneous adsorption is enhanced, resulting in prolonged retention.

A linear 10 minutes gradient ranging from 100% DCM to 100% dimethylformamide (DMF) was employed on a polar stationary phase to separate PPDOs according to their end groups. Under the chromatographic conditions chosen the PPDO-diol samples showed two separated peaks. The characterization of the chromatographic

fractions using matrix assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF-MS) revealed the first peak to contain PPDOs with two OH end groups as the predominant structure. The MALDI-TOF spectra for the second peaks showed three different series. The masses of the three series were consistent cyclic PPDOs, PPDOs carrying one carboxyl and one OH end group and PPDOs having one Li-carboxylate and one OH end group.

To gain insight into the chemical heterogeneity of the MBCs samples a gradient method was developed. The method allowed separating PPDO-diols and PPDO-multiblock polymers (MBP) from the PCL-diols and the PCL-MBPs. MBPs were derived by linking either PCL- or PPDO-diols with a diisocyanate. The application of the developed gradient to the MBC-samples resulted in two well separated main peaks. The first peak eluted in SEC mode before the start of the gradient in the retention range of the PPDO-diols and the PPDO-MBPs. Since at the start of the experiment the eluent promotes adsorption of PCL, the retention volume of the first peak therefore suggests the existence of purely PPDO containing structures in the MBC-samples. The second peak eluted at retention times similar to PCL-diols and PCL-MBPs. Since in gradient chromatography the retention of a block copolymer is mainly determined by the chemical structure of the adsorbing block, a homopolymer of the same chemical structure than the adsorbing block is expected elute close to the block copolymer. Thus, based on the retention time of the second peak in gradient chromatography, this peak might consist of only PCL containing structures and/or the true multiblock copolymer.

In order to clarify whether the second peak contains true multiblock copolymer structures or only PCL containing structures (diols and MBPs), liquid chromatography under critical conditions (LCCC) for PCL was applied. On a reverse phase column critical conditions for PCL were achieved at 76% acetonitrile (ACN) and 24% DCM. Under these conditions PPDO containing structures are expected to elute before the void volume. Purely PCL containing structures are expected to elute at the void volume. Analysis of the MBC-samples at critical conditions revealed two main peaks in all chromatograms. Based on the elution volume the first peak is assumed to result from PPDO-diols, and/or PPDO-MBPs and/or MBCs. The second peak, eluting at the void volume, was assigned to "pure" PCL and/or PCL-MBP.

According to the chromatographic results it can be concluded that the MBCs contain significant amount of purely PPDO-containing (gradient chromatography) as well as purely PCL-containing (LCCC) structures. However, the existence of MBCs cannot be excluded based on the experiments so far, since the MBCs are expected to coelute with MBPs or diols in both of the chromatographic modes.

In order to validate the assignments of the peaks of the gradient chromatography and to find out about the existence of MBC-structures, identification of the peaks was conducted by means of off-line Fourier Transform Infrared (FTIR). The FTIR spectrum of the first peak revealed the characteristic absorption bands of PPDO while the bands characteristic for PCL were absent, indicating the presence of only PPDO-structures. The FTIR-spectrum of the second peak reveals the characteristic bands of PCL whereas the characteristics bands of PPDO were not found. This suggests that fraction 2 of the MBC from gradient chromatography consists mainly of PCL-units. These results therefore are in an agreement with the assignments based on the retention times. In addition the result indicates that peaks observed in gradient chromatography of the MBC-samples consist of purely PPDO- and purely PCL-containing structures. Accordingly the MBC-samples seem to be composed of PPDO/PPDO-MBP and PCL/PCL-MBP.

Since the results were rather unexpected, additional proof was aimed for. Pyrolysis gas chromatography/mass spectrometry (Py-GC-MS) was used as an alternative method to FTIR to verify the results. Gradient chromatography was used to fractionate the MBC-sample into two fractions, corresponding to the observed peaks. The resulting fractions were then analyzed by Py-GC-MS. Based on quantitative studies, the first peak of the gradient chromatography of the MBCs contained more than 80 % (wt%) of PPDO content whereas in the second peak of the gradient chromatography of the MBCs, 0-10% (wt%) of PPDO were found.

The results of the Py-GC-MS and FTIR studies on the fractions are qualitatively in good agreement. They clearly proof a strong difference in chemical composition of the two peaks in gradient chromatography. However, the quantitative results differ. According to the results of FTIR the peaks contain either PPDO- or PCL units, while Py-GC-MS detects smaller amounts of the respective other polyester in each peak.

Further characterization of fractions 1 and 2 of the gradient chromatography of the MBCs was performed by proton nuclear magnetic resonance ($^1\text{H-NMR}$). Quantitative $^1\text{H-NMR}$ -studies conducted on the two fractions showed that the first fraction contains more than 80 % (wt %) of PPDO, while the second fraction contains 20% (wt %) of PPDO. The $^1\text{H-NMR}$ results are therefore in qualitative an agreement with Py-GC-MS results. They showed that the peak 1 of the gradient chromatography of the MBCs is predominantly composed of PPDO-units, while the peak 2 of the gradient chromatography of the MBCs consists mainly of PCL-units.

From the results above it can be concluded that the MBCs under investigation are very heterogeneous. Thus, these results were valuable since they led to optimize of the synthesis conditions of the MBCs in order to reduce the chemical heterogeneity

7. List of Abbreviations and Symbols

ACN	Acetonitrile
ATR	Attenuated Total Reflection
C	Sample concentration
CCD	Chemical composition distribution
CHCl ₃	Chloroform
DCM	Dichloromethane
DMAc	N, N'-dimethylacetamide
DMF	Dimethylformamide
ELSD	Evaporative Light Scattering Detector
F	Flow rate
FTD	Functionality type distribution
FTIR	Fourier Transform Infra Red
Ge	Germanium
GLC	Gradient Liquid Chromatography
He	Helium
HFIP	Hexafluoroisopropanol
HPLC	High Performance Liquid Chromatography
IUPAC	Union of Pure and Applied Chemistry
K_d	Distribution coefficient
K_{LAC}	Contribution of adsorption to distribution coefficient
K_{SEC}	Contribution of size exclusion to distribution coefficient
LAC	Liquid Adsorption Chromatography
LC	Liquid chromatography
LC-CC	Liquid Chromatography at Critical Conditions
MALDI	Matrix-Assisted Laser/Desorption Ionization
MBC	Multiblock copolymer
MBP	Multiblock polymer
\overline{M}_n	Number average molar mass
\overline{M}_w	Weight average molar mass
MWD	Molar mass distribution

NMR	Nuclear Magnetic Resonance
PCL	poly (ϵ -caprolactone)
PDI	Polydispersity Index
PDO	1,4-dioxane-2-one
PPDO	poly (p-dioxanone)
PU	polyurethane
Py-GC-MS	Pyrolysis Gas Chromatography Mass Spectrometry
r	Ratio
R	Gas constant
RP	Reverse Phase
SEC	Size Exclusion Chromatography
SMA _s	Shape memory alloys
SME	Shape memory effect
SMM _s	Shape memory materials
SMP _s	Shape memory polymers
T	Absolute temperature
T _g	Glass transition temperature
%T	Transmission
THF	Tetrahydrofuran
TIC	Total ion chromatogram
TMDI	Trimethyldiisocyanate
t_R	Retention time
V_0	Hold-up volume of the system
V_i	Column interstitial volume
V_d	Dwell volume
V_p	Pore volume of the HPLC column
V_R	Retention volume
ΔG	Free Gibbs energy difference
ΔH	Change in adsorption enthalpy
ΔS	Change in conformational entropy

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Eidesstattliche Erklärung

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbständig und nur mit den angegebenen Hilfsmitteln angefertigt und noch keine Promotionsversuch unternommen habe.

Darmstadt, den 03 December 2009

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