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Polymer 43 (2002) 2663–2669

polymer

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Preparative fractionation and characterization of polycarbonate/eugenol-siloxane copolymers

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Received 23 August 2001; accepted 28 December 2001

Abstract

Bisphenol-A polycarbonate/eugenol-siloxane copolymers were fractionated at the preparative scale by the continuous polymer fractionation (CPF) technique. It is the first example of copolymer fractionation by CPF. The distribution of siloxane species across the fractions was assessed for copolymers differing in initial siloxane concentration and block length. On- and off-line combinations of size exclusion chromatography and infrared spectroscopy were used to analyze chemical composition (CC) of the unfractionated samples across the molecular weight distribution enabling comparison with the fractions. A polycarbonate–siloxane copolymer containing 10 wt% of very short siloxane blocks (dp = 2) was fractionated solely according to molecular weight (MW). By contrast, a copolymer containing 5 wt% siloxane blocks with a larger degree of polymerization (dp = 23) was fractionated according to MW, as well as to CC. This 'chemical drift' effect for the larger siloxane block length can be ascribed to large solubility differences of low MW chains, which drastically vary in composition according to the (small) number of siloxane blocks they contain. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Bisphenol-A; Siloxane

1. Introduction

Polycarbonate–siloxane (PC–Si) copolymers were first introduced in the mid 1960s [1,2]. This class of copolymers is characterized by an outstanding thermal stability, good weathering properties, excellent flame retardancy, and high impact resistance at low temperature [3–7]. PC–Si materials are now used in numerous applications including windows, roofing, contact lenses, and gas-permeable membranes. A large group of bisphenol end-capped oligo-siloxanes are known to form useful copolymers with polycarbonate. A particularly interesting polysiloxane block is obtained by reacting hydrosilane-capped oligo-dimethylsiloxane with eugenol (4-allyl-2-methoxyphenol) using the well-known hydrosilation reaction. Eugenol is readily available as a synthetic or natural product. The resulting bisphenol-capped polysiloxane can be copolymerized with bisphenol-A to form a PC–Si copolymer [8,9]. The general structure of a PC/eugenol-siloxane (PC–EuSi) copolymer is shown in Fig. 1. PC–Si copolymers can be made via different synthetic routes including interfacial phosgenation and melt polymerization processes [3]. Depending on the siloxane block length and domain size, the copolymers are transparent, translucent or opaque [3,7].

In general, properties of copolymers are mainly determined by their overall composition, microstructure (e.g. statistical, graft or block copolymer), and structural heterogeneity. Structural variation across the molecular weight distribution (MWD) can be studied by fractionation [10]. If fractions are to be used for further analysis, fractionation is to be performed on a preparative scale. Determination of rheological, mechanical, and flame-retardant properties, for instance, require significant amounts of test-material. Most common fractionation methods, however, deliver fractions of analytical size (mg) only.

Continuous polymer fractionation (CPF) has been especially developed to produce large size fractions in a relatively short time frame. Many classes of homopolymers have been successfully fractionated using CPF including polyolefins, polysiloxanes, and polyesters [11,12]. The technique has never been applied previously for the fractionation of copolymer materials. CPF is based on a continuous liquid–liquid extraction in a counter-current process, where fractions are removed from a concentrated polymer solution (feed) by a single solvent or solvent/non-solvent mixture (extracting agent). The feed and the extracting agent are introduced into a column, where the two phases that evolve

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0032-3861/02/$ - see front matter
PII: S0032-3861(02)00052-6

from them are transported against each other due to their different densities. Low molecular weight (MW) material extracted from the polymer-rich phase by the extracting agent forms the sol fraction, while the remaining higher MW material forms the gel fraction. Preparatory experiments for CPF include determination of the miscibility gap for the ternary system by measuring cloud points and construction of tie-lines by demixing experiments.

In this paper, we report for the first time an example of copolymer fractionation at the preparative scale by the CPF method. The general applicability of CPF for the fractionation of copolymers has been assessed. A primary objective was to study the distribution of siloxane species across the MWD for two PC–EuSi samples. The experimental study involves fractionation followed by analytical characterization of the fractions. These results have been compared with characterization of the original samples by coupling of SEC and IR spectroscopy. Besides structure characterization, a major objective of the fractionation experiments was to obtain large size fractions to be used for further chemical and physical testing. This aspect will be the subject of future publications.

2. Experimental

2.1. Samples

Two lab synthesized PC–EuSi copolymers (PC-SIL1 and 2) made by interfacial phosgenation have been kindly provided by GE Plastics, Bergen op Zoom, The Netherlands. PC-SIL1 contains 10 wt% eugenol-capped siloxane oligomer with a degree of polymerization of 2 ($n = 0$ on average in Fig. 1) and PC-SIL2 contains 5 wt% eugenol-capped siloxane oligomer with a degree of polymerization of 23 ($n = 21$ on average in Fig. 1).

2.2. Continuous polymer fractionation

2.2.1. Equipment

CPF experiments are carried out with a fractionation device combining two glass columns with independent temperature control. The larger column is completely filled with a 1:1 mixture of glass beads of 8 and 10 mm diameter, respectively. For the smaller column, the ratio is 3:1 and the beads diameters are 6 and 8 mm. The feed inlet is positioned between the columns at approximately three-fourths of the total height of the system. The extracting agent inlet is positioned at the bottom of the fractionation device. Two piston pumps are used for regulation of feed and extracting agent fluxes. Glass reservoirs are used for supply of feed and extracting agent. A large CPF set-up (total column length = 2.40 m, inner diameter = 3.5 cm) is used for the fractionation of PC-SIL1, while a smaller version (total column length = 1.90 m, inner diameter = 1.5 cm) is used for the fractionation of PC-SIL2.

2.2.2. Solvents

Methylene chloride (MCH): Roth, >99%, synthesis grade; Diethylene glycol (DEG): Acros, 99%.

2.2.3. Construction of the ternary phase diagram

In order to construct the ternary phase diagram, cloud point curves are recorded at room temperature (20 °C) by titrating polymer solutions in MCH with DEG, until visible turbidity. Information about the demixing behavior of the solvent/non-solvent/polymer system is obtained by preparing compositions within the miscibility gap of the phase diagram and subsequent analysis of the conjugated sol and gel phases using proton-NMR. Tie-lines are constructed by connecting sol and gel compositions in the ternary phase diagram. The so-called working line connects feed and extracting agent compositions and is chosen in a way that it runs approximately parallel with the experimentally determined tie-lines. The feed composition has a high polymer concentration (10–15 wt%) and is positioned outside the miscibility gap at a distance of approximately 1 wt% from the cloud point curve.

2.2.4. Isolation of fractions

DEG is removed from collected fractions by repeated extractions with a 2-fold excess of water using a separation funnel, until the content in the fractions is lower than 20 ppm as determined by proton-NMR. Dichloromethane is subsequently removed by evaporation at 40 °C under reduced pressure by means of a rotation evaporator. It is confirmed by NMR and SEC that the applied isolation procedure has no influence on the chemical structure or MW of the fractions.

2.3. Batch fractionation

Collected volume of gel fraction for PC-SIL1 in run 3 is too small to apply CPF reasonably. Therefore, this material has been fractionated discontinuously by dropping the feed

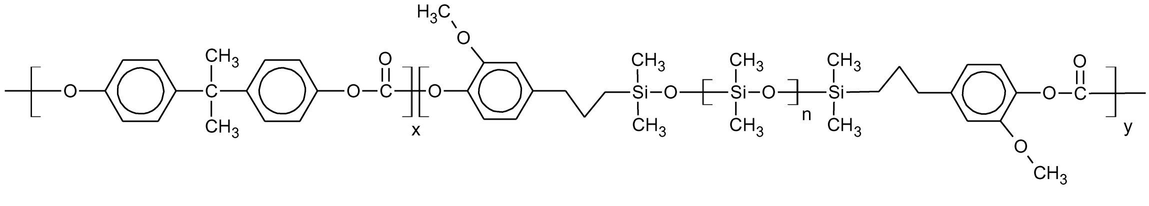

Fig. 1. General structure of a BPA-polycarbonate/eugenol-siloxane copolymer.

Table 1
Fractionation parameters for PC-SIL1 and PC-SIL2

	CPF run#	FEED (w1/w2/w3)[a]	EA (w1/w2)	Fractionation temperature (°C) column/condenser[b]	Fluxes (ml/min) (FEED/EA)	Fraction number (#): Yield (g) [S/G/C][c]
PC-SIL1	1[d]	0.800/0.060/0.140	0.785/0.215	21/8	1.2/3.8	#1: 24 [S]; #2: 12 [C]
	2[d]	On gel of run #1[e]	0.800/0.200	17/10	1.1/3.8	#3: 10 [C]; #4: 5 [G]
	3[f]	0.760/0.100/0.140[g]	0.750/0.250	Room temperature	FEED/EA: 1/10 (wt/wt%)	#5: 6 [S]; #6: 5 [G]
PC-SIL2	1[h]	0.815/0.055/0.13	0.805/0.195	21/8	1.2/3.7	#1: 5 [G]
	2[h]	0.815/0.055/0.13[i]	0.785/0.215	21/8	1.1/3.8	#2: 12 [S]; #3: 4 [C]; #4: 30 [G]

[a] w1 = methylene chloride, w2 = diethylene glycol, and w3 = PC–siloxane.
[b] Column and condenser are designations for the lower and upper columns of the fractionation device, respectively.
[c] Phase from which the PC fraction was isolated: S = Sol, G = Gel, and C = Column.
[d] CPF run: large set-up.
[e] PC-SIL1, CPF run #2 on gel obtained from CPF run #1.
[f] Batch fractionation run.
[g] PC-SIL1, run #3, batch fractionation on PC isolated from the sol fraction of CPF run #2.
[h] CPF run: small set-up.
[i] PC-SIL2, CPF run #2 on PC isolated from the sol fraction of CPF run #1.

slowly into a 10-fold surplus of a mixture of DEG and MCH. For more details, cf. Table 1.

2.4. Size exclusion chromatography

2.4.1. SEC–UV

SEC measurements on the fractions have been run on a Waters SEC system combined with a Waters 486 tuneable UV absorbance detector. PC–EuSi samples in MCH (0.1 wt/v%) containing 0.025% toluene as flow marker are filtered through 0.45 μ filters and injected on the SEC system at an injection volume of 50 μl. Two PL-gel 5 μ 300 × 7.5 mm^2 columns with pore sizes of 10^3 and 10^5 Å are used in series. MCH is used as mobile phase at a flow rate of 1.0 ml/min. The eluted polymer is detected at 254 nm. Calibration is performed against a series of monodisperse PS standards with known absolute MW.

2.4.2. On-line SEC–IR

On-line SEC–IR measurements have been run on a system consisting of a Waters WISP 712 autosampler, Model 590 pump, Model 441 Absorbance detector at 254 nm and a Miran 1A CVF IR monitor set at 9.5 μm (1053 cm^{-1}) with a filter time constant of 4 and 1 mm slit width. The flow rate is 1.0 ml/min of chloroform with 1% ethanol and the column bank consists of one Waters Microstyragel 500 Å and two PL 5 μm columns with pore sizes of 10^3 and 10^4 Å.

2.4.3. Off-line SEC–FTIR

The LC system consists of an HP1050 pump, injector and diode array detector along with an LC-Transform Series 400 interface. The solvent, flow rate, and column set are identical to those used for the on-line SEC–IR system. The LC-Transform sprays a track of the column effluent on the edge of a germanium disc, that is, coated on the backside with a reflective aluminium film. The disc is driven by a stepper motor at 10°/min and this produces a dry film of the non-volatile components around the edge of the disc. The disc is next transferred to a Nicolet Magna 550 FTIR fitted with a beam condenser and the same stepper motor drive as on the LC-Transform. Analysis is performed at 4 cm^{-1} resolution with 32 scans per sample and a step size of 2°/spectrum. With the collection rate of 10°/min, this works out to 12 s of retention time per spectrum.

2.5. NMR

2.5.1. Proton-NMR

Proton-NMR measurements are obtained on a Bruker Avance 400 spectrometer using a 5 mm i.d. Quadro Nuclei Probe. A pulse width of 90° (10 μs), relaxation time of 4 s and acquisition time of 2.6 s are used. Sol and gel phases obtained from demixing experiments for determination of tie-lines are prepared at a concentration of 5 wt/v% in d-chloroform. One hundred and twenty eight free induction decays (FIDs) are collected for compositional analysis of the phases. CPF fractions are dissolved in d-chloroform at a concentration of 5–10 wt/v%. One thousand and twenty four FIDs are collected for analysis of the fractions. The siloxane block length is calculated using the areas of the siloxane-dimethyl and siloxane–eugenol-methoxy proton absorbances at 0.04 and 3.79 ppm, respectively. The siloxane content is determined using the PC-methyl absorbance at 1.50 ppm and siloxane–eugenol-methoxy proton absorbances. A complete removal of DEG from the fractions is necessary as it interferes with the siloxane-methoxy absorbance in the NMR spectrum.

2.5.2. ^{13}C-NMR

Equipment is similar as for proton-NMR. A pulse width of 30° (4.3 μs), relaxation time of 5 s and acquisition time of 1.5 s are used. Samples are dissolved at a concentration of 15 wt/v% in d-chloroform. For analysis of the copolymer

Table 2
Theoretical and experimental dyad mol fraction composition for PC-SIL1 and PC-SIL2 as determined by ^{13}C-NMR

Sample	^{13}C-NMR	
	Theoretical ratio[a] BB/BS/SS[b]	Measured ratio BB/BS/SS
PC-SIL1	0.886/0.111/0.003	0.878/0.122/$<$0.005[c]
PC-SIL2	0.986/0.014/5×10^{-5}	0.984/0.016/n.d.

[a] Expected ratio of dyad fractions for a statistical copolymer.

[b] B = BPA, S = eugenol siloxane.

[c] No accurate quantification possible.

microstructure, 30.000 FIDs are collected. Dyad mole fractions are determined from the integrated carbonate resonances at 151.8 (BPA–BPA), 151.5 (BPA–siloxane) and 151.3 (siloxane–siloxane) ppm, respectively.

3. Results and discussion

3.1. Fractionation of samples

The fractionation of copolymers presents a special problem. For a chemically homogeneous polymer, solubility depends on MW only. In the case of chemically inhomogeneous materials, such as copolymers, solubility is determined by MW, as well as by chemical composition (CC). In the case of copolymers, both the MW and CC can change during the course of fractionation. In addition, copolymers with the same overall CC, but differing in microstructure might have a different solubility behavior. If the effect of CC is negligible against the effect of MW, fractionation can be carried out analogously to the fractionation of a homopolymer. If both CC and MW influence fractionation, changes in temperature or solvents may lead to different results and fractions are obtained that differ in MW, as well as CC [13]. Fractionation results should therefore always be cross-checked by a second analytical method.

Previous CPF studies have shown that a MCH/DEG solvent/non-solvent mixture is a suitable candidate system for linear and lightly branched BPA–PC materials [14,15]. After orienting experiments, it was also selected as the best solvent system for fractionation of the copolymers investigated here. PC–siloxane copolymers are prone to hydrolysis [16], which is prevented by using the MCH/DEG system. In addition, crystallization of low MW fractions in the fractionation column is avoided. As part of the preparative work for CPF experiments, the MCH/DEG/PC-SIL ternary phase diagram was constructed by measuring cloud point curves and determining tie-lines. The determination of tie-lines appeared to be particularly difficult for PC-SIL2 as phase separation occurred very slowly. This could be the result of an emulsifying action of the PC-SIL copolymers resulting from their polar–apolar microstructure. For PC-SIL2, CPF parameters optimization, such as a well controlled fractionation temperature and accurately selected feed and extracting agent compositions appeared to be especially important.

Two similar CPF set-ups were used for the fractionation of PC-SIL1 and PC-SIL2 only differing in dimensions. After each fractionation step, a high MW gel fraction, a low MW sol fraction and a remaining column fraction were collected. For subsequent fractionation steps, either the gel or sol phase was used directly or after isolation of the polycarbonate fraction. The final fractionation run for PC-SIL1 was accomplished by applying a batch fractionation method. PC-SIL1 and PC-SIL2 were fractionated into six and four fractions, respectively. Samples were fractionated at a rate of 5–15 g/h. Fractionation parameters are given in Table 1.

3.2. Characterization of unfractionated copolymers

Microstructure of the unfractionated copolymers was determined using ^{13}C-NMR. Carbon absorbances resulting from the carbonate group were used for quantification purposes. The measured dyad composition for PC-SIL1 and PC-SIL2 is very close to the theoretical composition for completely statistical copolymers. Results are shown in Table 2. While PC-SIL1 is a statistical copolymer in the literal sense of the word, PC-SIL2 can better be looked upon as a segmented copolymer with a statistical distribution of siloxane blocks.

The distribution of siloxane species across the MWD was assessed using on- and off-line SEC–IR hyphenating techniques. An important advantage of the off-line technique is that the sensitivity of the measurement can be significantly increased by collecting polymer fractions of consecutive SEC runs. The inherent sensitivity of an on-line IR detector is rather low, which often results in a noisy response, even for peaks that usually have a strong absorbance in the IR region.

Using off-line SEC–FTIR, following LC separation, the copolymers were analyzed for peak height at 1051 cm^{-1} for the siloxane and at 1082 cm^{-1} for the BPA–PC component. A plot of peak intensity versus time is called a chemigram. The chemigram for PC-SIL2 is shown in Fig. 2. BPA–PC and siloxane peaks show complete overlap indicating no significant composition drift across the MWD.

On-line SEC was used as a confirmatory technique. The on-line SEC chromatogram for PC-SIL2 comprising of UV (BPA–PC) and IR (siloxane) traces is shown in Fig. 3. Also here, BPA–PC and siloxane traces overlap completely across the entire MWD confirming off-line SEC–IR findings.

For PC-SIL1, similar results were obtained, i.e. a complete overlap of BPA–PC and siloxane traces as determined by both on- and off-line SEC–IR techniques.

These combined results indicate that the siloxane blocks of both copolymers are statistically distributed on chains of all lengths.

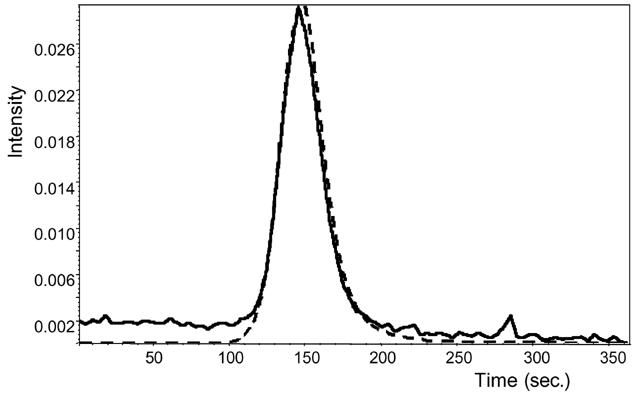

Fig. 2. Off-line SEC–IR chemigrams for BPA-polycarbonate (dotted line) and eugenol-siloxane (solid line) of PC-SIL2.

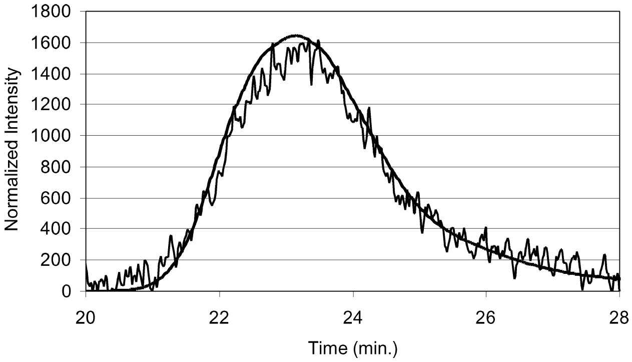

Fig. 3. On-line SEC–IR/UV chromatogram for PC-SIL2: smooth line = UV response (PC detection); noisy line = IR response (siloxane detection).

3.3. Characterization of fractions

MW results from SEC–UV are shown in Table 3 (as equivalent PS MW). A SEC–UV overlay plot of the PC-SIL1 and corresponding fractions MWD is shown in Fig. 4. Only a limited number of fractions are depicted for clarity. It is important to keep in mind that SEC separates polymer chains based on differences in hydrodynamic volume. In the case of chemically heterogeneous polymers, like many copolymers and branched homopolymers, it cannot be simply assumed without further checking that SEC separates chains according to MW exclusively. Copolymer molecules with different MW can have the same hydrodynamic volume due to differences in their chemical microstructure. However, this problem is not serious for the samples studied here, since CC is homogeneous across the MWD as demonstrated by the SEC–IR results.

Siloxane contents and block lengths of the fractions were determined using proton-NMR. Fig. 5 shows how the siloxane concentration depends on the fraction number average MW for the investigated copolymers. For PC-SIL1, the measured siloxane concentration is constant for all fractions and the unfractionated polymer. For PC-SIL2, the siloxane content decreases with increasing MW of the fractions. This result implies a CC drift during fractionation, since we know there is no such dependence for the original sample. On first sight, there is a contradiction between the NMR/SEC–IR findings that PC-SIL2 is compositionally homogeneous and that fractions vary in siloxane concentration. The statistical nature of PC-SIL2 should lead to fractionation according to MW only. However, it can be derived from SEC and NMR data that for all fractions, the number of siloxane blocks built in PC-SIL2 chains is very low (less than three on the average). This means that many polymer chains are free of siloxane blocks or contain a very small number of them. The solubility differences between chains containing no versus one or several siloxane blocks is probably responsible for the CC drift during fractionation. This effect is especially pronounced for low MW chains. Since the solubility of PC–EuSi copolymers is higher in MCH/DEG mixtures than the solubility of pure PC (as could be concluded from orienting dissolution experiments), it is logical that a higher than average siloxane content is found in the low MW fractions, which are extracted in the DEG-rich sol phase and a lower than average siloxane content in the high MW fractions,

Table 3
Characterization data for PC-SIL1 and PC-SIL2 (data are listed in order of fractionation rather than in order of MW)

	Sample	SEC–UV			Proton-NMR	
		M_w (g/mol)	M_n (g/mol)	D	Siloxane (wt%)	Siloxane block length
PC-SIL1	Total	49,400	21,200	2.33	10.1	2.2
	Fraction 1	24,100	11,500	2.10	10.1	2.3
	Fraction 2	25,300	13,700	1.85	10.1	2.3
	Fraction 3	27,500	14,100	1.96	9.8	2.3
	Fraction 4	72,700	50,400	1.44	9.7	2.3
	Fraction 5	16,700	9,700	1.72	10.1	2.3
	Fraction 6	37,900	26,200	1.45	9.6	2.4
PC-SIL2	Total	69,600	24,800	2.81	5.3	23.3
	Fraction 1	87,100	52,300	1.67	4.0	22.1
	Fraction 2	25,300	11,100	2.28	8.0	24.8
	Fraction 3	31,000	12,300	2.51	7.0	24.8
	Fraction 4	66,800	38,900	1.71	4.3	23.0

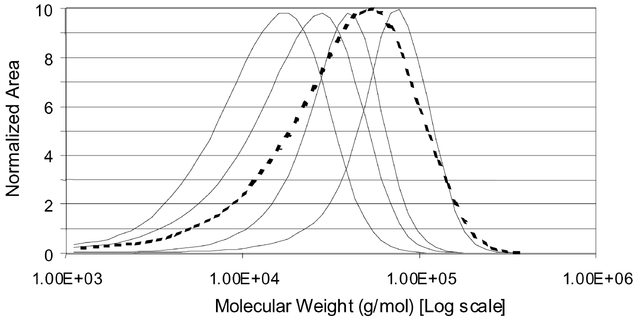

Fig. 4. SEC–UV overlay plot for PC-SIL1: unfractionated polymer (dotted line) and fractions 2, 4, 5 and 6 (solid lines).

which are extracted in the MCH-rich gel phase. The observed CC drift is thus the combined result of two causes: differences in solubility as function of composition and presence of chains with significant differences in composition due to the low number of siloxane blocks per chain, despite the statistical nature of the copolymer microstructure.

Fig. 6 shows the evolution of average siloxane block length as a function of number average MW for both copolymers. For PC-SIL1, the block length is constant for all fractions and the unfractionated polymer. In the case of PC-SIL2, the block length decreases with increasing MW of the fractions. Expressed in absolute number of siloxane units per block, this decrease is rather limited, but in line with the finding that siloxane content varies as a function of fraction-MW. A similar reasoning can be applied as for siloxane concentration: even a small variation in block length will have a large influence on solubility, especially for short chains.

The SEC–IR results obtained for the unfractionated polymer, i.e. no composition drift across the MWD, as well as characterization results for the fractions, i.e. constant siloxane concentration and block length across the MWD, indicate that PC-SIL1 is fractionated solely according MW. Characterization results for PC-SIL2 indicate that this sample is fractionated according to MW, as well as CC.

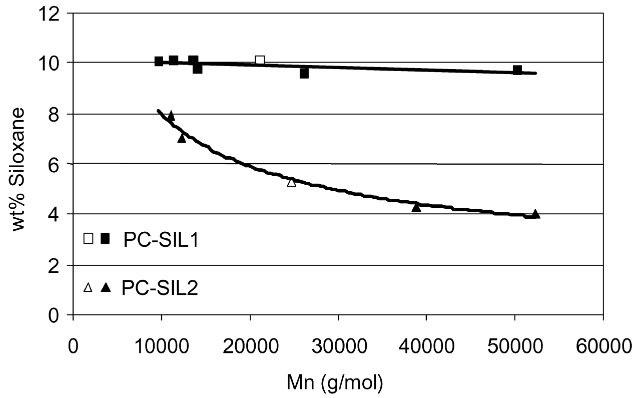

Fig. 5. Siloxane concentration as a function of the number average MW for PC-SIL1 and 2; closed symbols denote the fractions, open symbols the initial unfractionated polymer.

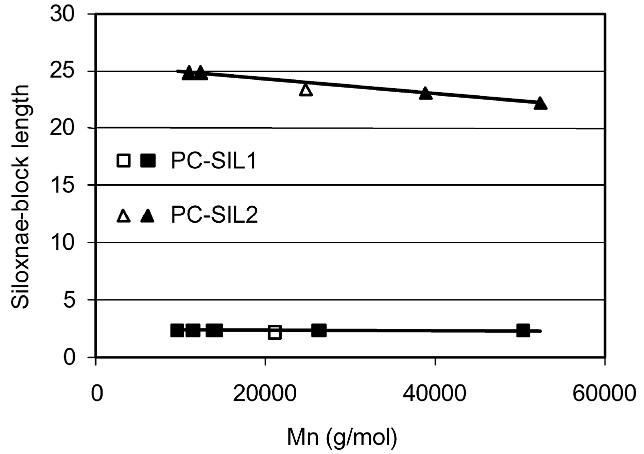

Fig. 6. Siloxane block length as a function of the number average MW for PC-SIL1 and 2; closed symbols denote the fractions, open symbols the initial unfractionated polymer.

4. Conclusions

The CPF technique was used to fractionate segmented PC–EuSi copolymers with different block lengths on the preparative scale.

Large size fractions were obtained that can be used for further analysis, e.g. rheological and mechanical testing and determination of flame-retardant properties.

The distribution of siloxane species across the MWD is homogeneous for a copolymer containing very short (dp = 2) siloxane blocks. A copolymer comprising larger siloxane blocks (dp = 23) was fractionated according to MW and CC simultaneously. The observed CC drift for the latter copolymer is ascribed to the combination of two factors: (i) copolymer composition-dependent solubility in the solvent mixture used for fractionation and (ii) a low number of siloxane segments per chain, resulting in chain populations with different compositions, despite the statistical distribution of comonomer segments.

The contrasting behavior of the two copolymers studied highlights the applicability and limits of CPF for copolymers. Obviously, chemical heterogeneity of the copolymer combined with composition-dependent solubility is the issue. Our results show that copolymers with statistically distributed segments can be fractionated by MW using CPF only to the extent that all chains have the same average composition, which is not the case for short chains carrying a small number of long comonomer segments.

Similar influence of chain ‘individuality’ on properties of statistical copolymers has been observed before in the case of PET [17]. The low concentration of DEG units in PET results in distinct chain populations according to the maximum length along the chain with no DEG ‘defects’. This dramatically affects crystallization and melting as evidenced by temperature rising elution fractionation (TREF) and DSC techniques.

Acknowledgements

The authors would like to thank Dr J.C. Carnahan of GE Corporate Research and Development, Schenectady, NY, USA, for carrying out the SEC–IR analyses.

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