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Characterization of the PMMA- and PEO-, di- and triblock copolymers, by light scattering, SEC and vapour pressure osmometry

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Abstract

The aggregation of block copolymer dissolved in methyl ethyl ketone (MEK) as well as toluene was observed. The aggregation of molecules leads to micelles and clusters of micelles. Between micelles and clusters a dynamical equilibrium exists. Inside the micelles lyophobic chains of PEO are combined and the outer layer of micelles is formed by lyophilic chains of PMMA. This is observed particularly in samples with triblock or diblock structure and high portions of PEO. In these cases, there are great differences between molecular weights obtained by light scattering, SEC or vapour pressure osmometry (VPO). We introduce a factor A to study the relation of the PEO content in diblock or triblock structure, and the measured M_w . © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Block copolymers containing poly(ethylene oxide) (B,C,D) and poly(methyl-methacrylate) (A) were investigated. The samples used had a diblock or triblock structure of the type A-B(C,D) or A-B(C)-A. The PEO-blocks had a molecular weight of 1000 (B), 2000 (C) and 5000 g/mol (D). The PMMA-blocks had varying molecular weights (Table 1). The copolymers are soluble in toluene, acetone, tetraline, tetrahydrofuran (THF), chloroform and methyl ethyl ketone (MEK). Samples with a higher molecular weight of PEO than PMMA are water soluble. According to their behaviour in solution, polymers containing PEO and PMMA are regarded as non-ionic amphiphiles. In MEK, PMMA-blocks are lyophilic and PEO-blocks are lyophobic.

The aim of this work was to determine the molecular weight and molecular weight distribution of differently composited PEO- and PMMA-block copolymers. It was also important to find a model for the structures formed in solution. We compared calculated M_n and measured M_n . To study the micelle formation, it is useful to apply size exclusion chromatography [1], light scattering and UV spectroscopy.

2. Experimental

The block copolymers were synthesized by group transfer polymerization of MMA using PEO-macroinitiators. PEO-macroinitiators were prepared from PEO-methacrylates, by the addition of dimethylethylsilane in the presence of a Wilkinson catalyst under an argon atmosphere. The reactions were carried out in THF at 35°C for 48 h. All block copolymer syntheses were carried out under the high purity conditions required for living polymerizations. A typical experiment is given below. A calculated amount of the PEO-macroinitiator in THF was filled in the reaction flask via a syringe. Then a portion of Tris(dimethylamino)sulfonium bifluoride (TASHF$_2$; solution in THF) was added as a catalyst. The TASHF$_2$ quantity was based on the silyl ketene acetale end-groups of the macroinitiator. After mixing at room temperature for 5 min, the MMA monomer was slowly added via a syringe. After 20 min, the polymerization was terminated with methanol/HCl to hydrolyse the trialkyl-silyl group. The polymer was precipitated in petroleum ether, extracted with water, and dried in vacuum at 40°C [2]. The reaction is outlined in Scheme 1.

Differential scanning calorimetry (DSC) investigations (DSC-30, METTLER) showed that the glass transitions of PEO and PMMA depend on the composition of the block copolymers. Triblock copolymers showed a glass transition

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Table 1
Characteristics and nomenclature of the used polymers (molecular weight determination on annealed samples, 15 h at 40°C)

Samples	PEO (g/mol) B,C,D	PMMA (g/mol) A	T_G PEO (°C)	T_G PMMA (°C)	VPO M_n 37°C (g/mol)	SEC M_n (g/mol)	SLS ZIMM M_w (g/mol)
AC 1/1	2000	1000	− 34.1	—	3120	—	106 200
AC 1/2	2000	2000	− 34	35.7	4770	—	38 000
AC 1/3	2000	3000	—	50.6	8030	9400	27 200
AC 1/6	2000	3000	—	65.8	15 000	14 700	24 400
AC 1/7	2000	2000	—	51	10 200	11 000	14 600
AD 1/1	5000	2000	− 42	—	5300	—	16 000
AD 1/2	5000	3000	—	20.1	8830	10 000	27 200
AD 1/3	5000	5000	− 40.8	—	3080	10 500	29 300
AD 1/4	5000	8000	− 43.7	20.2	11 500	13 300	35 300
ABA 1/6	1000	4100	− 34.1	34.7	2450	6100	27 800
ABA 7/1	1000	3000	—	44.3	4140	6200	23 000
ABA 7/2	1000	4000	—	49	4030	6000	44 800
ACA 2/1	2000	1000	− 59.2	—	2940	—	478 000
ACA 2/2	2000	2000	− 34.1	16.5	2330	5200	48 500
ACA 2/3	2000	4000	—	57.9	7910	12 000	34 000

shift to lower temperatures. In the temperature interval from 35°C to 50°C, crystalline lamellae of PEO in the block copolymer melt ($F_P = 50$°C–52°C at 2000 g/mol). The amorphous MMA-layers disturbed the crystalline order of PEO.

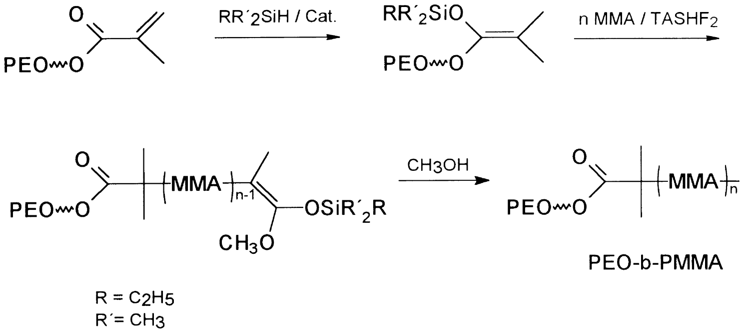
A distinct weight loss was observed by thermogravimetry at 30°C. This loss may be traced back to petroleum ether used to purify the polymers. The slight weight loss at 200°C is based on bound crystal water.

The SEC measurements (WATERS) were carried out with THF as an eluent. The flow rate was 1 ml/min. The styragel columns used had an average pore diameter of 1000 Å, 10 000 Å and 100 000 Å. An RI detector (refractive index) and a UV detector (diode-array or fixed wavelength $\lambda = 228$ nm) were used. At $\lambda = 228$ nm we were able to explain the chromatograms. The evaluation of the molecular weight was based on a PMMA calibration curve combined with a poly(styrene) (PS) calibration curve at a lower-molecular range (< 700 g/mol). The modified calibration curve was fitted by a polynome of 5th degree (correlation coefficient $r = 0.9997$). It is appropriate to extend the PMMA calibration curve with values of PS calibration standards, because the hydrodynamic volume did not influence the separation process in the pores of columns in this range. For PS, the individual oligomer, heptamer, hexamer and pentamer were resolved, and could be used in the calibration. In comparison, retention times of PMMA homopolymers (standard of calibration) and PS homopolymers (standard of calibration) indicate that PMMA, in spite of good solubility in THF, has more flexible chains. From this, it can be concluded that PMMA remains inside the columns for longer and has a higher retention time than PS.

The solution recovered samples show differences when compared with the chemically identical samples, which were only annealed. Hence, in the lower molecular range a broadening of peaks was observed.

The number average molecular weights (M_n) were determined by vapour pressure osmometry (KNAUER) in toluene, THF and MEK at 37°C and 50°C. MEK is a good solvent for these block copolymer systems.

Light scattering values were obtained in MEK using a modified SOFICA 42 000 at a wavelength of $\lambda = 633$ nm [3,4]. In order to accomplish particle size, analysis equipment from TOPAS was used. The principle of this method is the determination of the scattering intensities of single particles, in a free falling liquid jet with hydrodynamic focussing through a laser light sensor (perpendicular to the incident light beam). The scattering intensity depends on



Scheme 1.

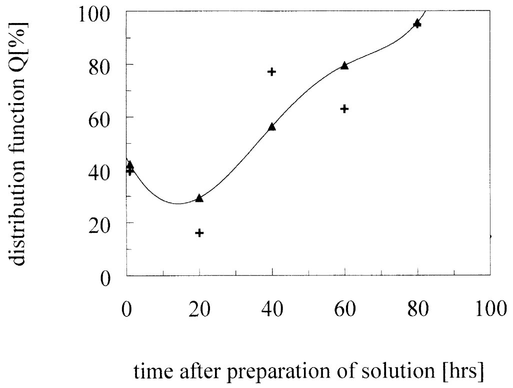


Fig. 1. Particle size determination in toluene; analysis at $x_i = 1\ \mu$m [8]: sample ABA 1/6 at different concentrations (+) 4 g/l and (▲) 6 g/l).

the size and shape of particles, as well as on the index of refraction of particles and the medium. The distribution function $Q_0(x_i)$ is the percentage of particles, which is smaller than the considered size of particles x_i [5].

3. Results

The particle size was determined in toluene and MEK. In toluene, the tendency of aggregate into clusters is very strong. Many particles exist with a size (x_i) greater than 1 μm. The measured particle size is time-dependent, but independent on the polymer concentration. The maximum of the particle size is achieved 20 h after preparation of the solution. After more than 20 h these large particles decayed (Fig. 1). We assumed that the polymer solution contains higher molecular weight particles (micelles and cluster of micelles) and residual polymer [6,7]. Between micelles and clusters a dynamical equilibrium exists. The value of equilibrium in MEK and toluene is 0.5 μm. The tendency to form clusters and micelles is greater in toluene than in MEK. Therefore, the portion of higher molecular weight particles in toluene is greater than in MEK (Fig. 1).

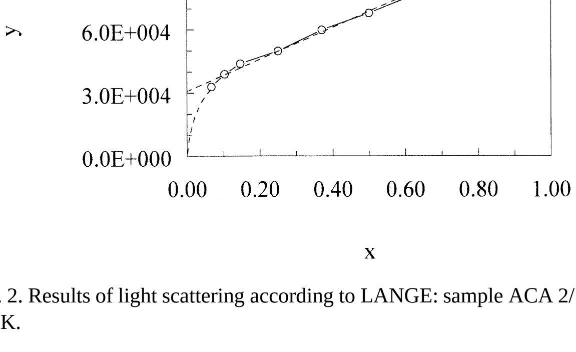


Fig. 2. Results of light scattering according to LANGE: sample ACA 2/1 in MEK.

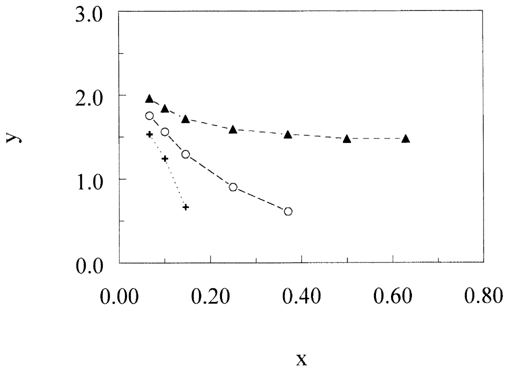


Fig. 3. Evaluation of results of light scattering according to GUINIER: sample AC 1/3 in MEK after 24 h waiting time (▲) summation scattering curve, (O) first difference and (+) second difference.

As a consequence of this behaviour, the resulting light scattering curve (ZIMM-plot) becomes very complex. The light scattering curve in toluene is more strongly bended downwards at small angles (30°–90°) than in MEK. Therefore, we found, for a sample solved in toluene, a weight-averaged molecular weight ($M_w > 10^6$ g/mol) which is much higher than for the same sample solved in MEK ($M_w < 10^6$ g/mol).

Thus, as the solvent for the determination of the molecular weights of the copolymers, MEK was used. The determined weight-averaged molecular weights (ZIMM-plot, Table 1) are high. The scattering curves are non-linear. Therefore, we evaluated the summation scattering curve by the model of Lange [9] (Fig. 2) and Guinier [10] (Fig. 3). The model described by Lange is based on the following equation:

$$x\cdot y = G + \gamma_2\cdot M_{2,\mathrm{W}}\cdot x, \tag{1}$$

with $x = \sin^2(\Theta/2)$ and $y = [(I_{\mathrm{red}})/(K\cdot c)]_{c\to 0}$. Accordingly, a dependence on x [the plot of $x\cdot y$] should be a straight line. The point of intersection with the y-axis represents G, the slope corresponds to the product of $\gamma_2\cdot M_{2,\mathrm{W}}$. By means of the linear part of the curve one can determine G, which is proportional to the content of high molecular weight particles γ_1 and the product of $\gamma_2\cdot M_{2,\mathrm{W}}$, which is proportional to the weight content γ_2 and to the molecular weight of the residual polymer $M_{2,\mathrm{W}}$ [9].

The scattering function introduced by Guinier:

$$P(\Theta) = \exp\left[-\frac{16\pi^2}{3\lambda^2}\cdot\langle r^2\rangle_z\cdot\sin^2\left(\frac{\Theta}{2}\right)\right], \tag{2}$$

is only valid at small angles and if

$$\sin^2\left(\frac{\Theta}{2}\right) \le 0.1125\cdot\left(\frac{\lambda}{n_A\cdot\langle r^2\rangle_z^{\frac{1}{2}}}\right) \tag{3}$$

If n chemically identical components are in solution,

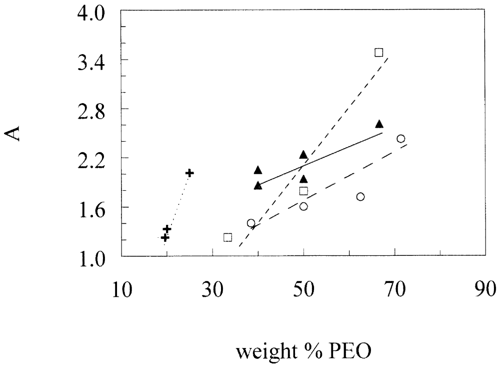


Fig. 4. Influence of the structure of the block copolymer and its PEO molecular weight on M_W [8]: (▲) diblock with $M_{PEO} = 2000$ g/mol, (○) diblock with $M_{PEO} = 5000$ g/mol, (+) triblock with $M_{PEO} = 1000$ g/mol, and (□) triblock with $M_{PEO} = 2000$ g/mol.

scattering is given by Eq. (4):

$$I_{red} = K \cdot \sum_i c_i \cdot M_i \cdot \exp\left[-\frac{16\pi^2}{3\lambda^2} \cdot \langle r^2 \rangle_z \cdot \sin^2\left(\frac{\Theta}{2}\right)\right]. \tag{4}$$

The $y = \lg I_{red}$ *versus* $x = \sin^2(\Theta/2)$ diagram shows a concave curve (Fig. 3). At large angles the curve approaches asymptotically the scattering function of the smallest molecules. A tangent on the curve corresponds to the scattering function of molecules with the smallest radius of gyration. Determining the difference of the total scattering function of the smallest molecules, one can also place a tangent to a resulting residual scattering function, i.e. the total scattering function is divided into the functions of partial scattering. From the slope of the tangents it is possible to calculate $\langle r^2 \rangle_z$. The intersection with the y-axis is equal to the product of concentration and molecular weight [10]. Scattering intensities of the sample AC 1/3 after 24 h, were used for the evaluation according to Guinier (Fig. 3).

In order to describe the aggregation behaviour of the different copolymers a parameter A was introduced. A is a ratio of the calculated M_w at small ($\Theta \le 90°$) and large angles ($\Theta \ge 105°$) (Eq. (5)).

$$A = \left[\frac{M_W \langle \Theta_{30°} - \Theta_{90°} \rangle}{M_W \langle \Theta_{105°} - \Theta_{150°} \rangle} \right] \tag{5}$$

We found a strong dependence of A on the molecular weight of PEO blocks and the structure of the whole block copolymer (diblock–triblock structure, Fig. 4).

4. Discussion

When MEK lyophobic PEO blocks, specially in triblock structure, are rearranged in the triblock structure to clusters of aggregated micelles, the factor A increases markedly. The polydispersity U according to Schulz is also strongly dependent on the structure of the block copolymers. The factor U increased remarkably with the existence of either a triblock structure, or more chains of PEO than PMMA in the polymer molecule (Fig. 4). The size of particles was investigated by particle size analysis and showed a strong dependence on time and solvent. The solution contains micelles and clusters of aggregated micelles. The micelles formed these clusters to a greater extent in toluene than in MEK. The number of these clusters decreased with an increasing waiting time. In the solution there was an dynamic equilibrium between the micelles and the clusters of aggregated micelles. The adjustment of this equilibrium is a function of time and is faster in MEK than in toluene. The outer layer of micelles is formed by lyophilic chains of PMMA. The structure in solution is dependent on the relative block size of lyophobic chains of PEO [11]. The results of the Guinier analysis correlated with the values of the particle size determination. In samples having chains containing more PMMA than PEO (for instance in sample AC 1/3), there is a greater arrangement of micelles into clusters (Fig. 3). The radius of the scattering mass of large particles, as well as the product of concentration and molecular weight, decreased with increasing time. The radius of the scattering mass of the residual polymer is only negligibly reduced with increasing time, whilst the product of concentration and the molecular weight remained constant. The results of SEC correspond with the results of VPO and light scattering measurements. The difference between M_n determined by VPO and the kinetically calculated molecular weight was confirmed by the SEC measurements. By means of the results of VPO with non- annealed samples having lower experimentally determined molecular weights than theoretically calculated, we were able to explain the influence of lower molecular substances on the number average molecular weight M_n. VPO measurements of samples annealed for 15 h at 40°C were in good agreement with kinetically calculated molecular weights. Increasing the temperature of measurement from 37°C to 50°C, the molecular weights of diblock-copolymers determined by VPO increased moderately by about 15% (Table 1). The analysis of the light scattering data was complicated by the presence of larger particles in the polymer solution. Similar results of micelle formation from poly(ethylene oxide)-, poly(propylene oxide)-, poly(-ethylene oxide)- and poly(styrene)-poly(ethylene oxide) are described in Refs. [12,13].

5. Conclusion

The aggregation of block copolymer dissolved in toluene as well as MEK was observed. The aggregation of molecules leads to micelles and clusters of micelles. Between micelles and clusters a dynamical equilibrium exists. The value of equilibrium is 0.5 μm in both MEK and toluene. Inside the micelles, lyophobic chains of PEO are combined and the outer layer of micelles is formed by lyophilic chains of PMMA. This is observed particularly in samples with diblock or triblock structure. In these cases, if there are more chains of PEO than PMMA in the block copolymer, there are large differences between molecular weights obtained by light scattering, SEC or VPO. Therefore, we introduce a factor A to study the relation of the PEO content in diblock or triblock structure and the measured M_w. We found a strong dependence of A on the molecular weight of PEO blocks and the structure of the whole block copolymer.

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References

[1] Vilenchik LZ, Barman S, Pathak CP. Strategies in size exclusion chromatography, ACS Symposium Series, Vol. 635, Washington, DC: 1996:328–346.

[2] Budde H, Höring S. 5. Berliner Polymeren-Tage, Potsdam, 1994.

[3] Schröder E, Müller G, Arndt K-F. Polymer characterization. Munich: Hanser, 1989.

[4] Arndt K-F, Müller G. Polymercharakterisierung. Munich: Hanser, 1996.

[5] Manual of ‘‘TOPAS’’, 1994.

[6] Huglin MB. Light scattering from polymer solutions. London: Academic Press, 1972.

[7] Gast AP, Vinson PK, Cogan-Farinas KA. Macromolecules 1993;26:1774–1776.

[8] Bogumil Th. Diplomarbeit, TU-Dresden, 1994.

[9] Lange H Kolloid-Z Z Polym 1979;240:747–755.

[10] Gruber E, Schurz J. Angew Makromol Chem (Vol. 29–30) (386) 1973:121–136.

[11] Mortensen K, Brown W. Macromolecules 1993;26 (16):4128–4135.

[12] Jada A, Hoffstetter J, Siffert B. Proceedings of the 30th Rencontre Moriond, 1995:41–46.

[13] Alexandridis P, Holzwarth JF, Hatton TA. Macromolecules 1994;27 (9):2414–2425.