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SCIENTIFIC PAPER

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THE USE OF SIZE EXCLUSION CHROMATOGRAPHY COUPLED WITH LIGHT SCATTERING FOR THE CHARACTERIZATION OF POLYMERS

Size exclusion chromatography coupled with multi–angle light scattering (SEC–MALS) was used to obtain molar mass, radius of gyration and their distributions of various types of polymers. We used SEC–MALS as one of the most sensitive techniques for the detection of small fractions of high–molar mass species to study (a) the association of polyurethanes in N,N–dimethylformamide considering the influences of composition, solution concentration and temperature, (b) the formation of block copolymer micelles in selective solvents and (c) the autooxidative degradation of substituted polyacetylenes in tetrahydrofuran.

Size exclusion chromatography (SEC) is an important technique used for the separation of macromolecules according to their hydrodynamic volume and for the determination of molar masses of polymers and their distributions. The molar masses determined by SEC are, however, relative and depend on the type of monodisperse polymer standards (usually polystyrene) used for column calibration. On the other hand, static light scattering gives the absolute value of the weight–average molar mass (M_w), the z–average root–mean–square radius or radius of gyration (R_g) and the second virial coefficient A_2 of a polymer sample. The combination of SEC and multi–angle light scattering (SEC–MALS) is thus a powerful technique by which the distribution and absolute values of the polymer molar–mass averages can be determined directly, without column calibration. The calculation follows the expression $K{\cdot}c/R_\theta = 1/M_w{\cdot}[1 + (1/3\,\lambda^2)\,16\,\pi^2{\cdot}R_g^2{\cdot}\sin^2(\theta/2)]$, where c is the polymer mass concentration in solution, R_θ Rayleigh ratio at the scattering angle θ, and K is the optical constant ($K = 1/\lambda_0\,N_A\,[4\,\pi^2\,n^2\,(dn/dc)^2]$; λ_0 is the wavelength in vacuum, n the solvent refractive index and dn/dc the refractive index increment). In addition, the scaling law, i.e., the relationship between the molar mass and size, provides information on the molecular conformation of the dissolved polymer [1,2].

The SEC–MALS method is one of the most sensitive techniques for the detection of small fractions of high–molar mass species and, as such, it is very suitable for studying the association and degradation of polymer chains in solution. In this work we report on the results of our recent studies: (i) the association of polyurethanes (PU) in N,N–dimethylformamide (DMF) solutions as a function of PU composition, solution concentration and temperature [3,4], (ii) the micellization of block copolymer polystyrene–*block*–poly(methyl methacrylate) (PS–PMMA) in 1,4–dioxane/cyclohexane selective solvent mixtures[5,6], and (iii) the autooxidative degradation of substituted polyacetylenes in THF solutions [7,8].

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EXPERIMENTAL

Materials and synthesis

Segmented polyurethanes (PU) with different chemical compositions were synthesized by a two–step procedure in DMF as 40% solutions; the chain extension reaction was catalyzed with dibutyltin dilaurate [9]. We used an aliphatic or aromatic diisocyanate (1,6–hexamethylenediisocyanate, HDI, or 4,4'–methylene–bis(phenyl isocyanate, MDI), a polyether diol – poly(tetramethyleneoxide), PTMO 1000, and a low molar mass diol as a chain extender (2,2–dimethyl–1,3–propanediol, synonym neopenthylglycol, NPG, and 2,2–bis(hydroxymethyl)propionic acid, synonym dimethylolpropionic acid, DMPA) in the molar ratio 3:1:2. The model compound, representative of PU soft segments, was synthesised using MDI and PTMO in the molar ratio 1:1 (designation MDI–PTMO). Non–carboxylated PU are designated as H–D0 and M–D0 (prepared with HDI or MDI, PTMO and NPG), while carboxylated PU are designated as M–D50, where '50' stands for the molar percentage of DMPA in the chain extender mixture.

All the polystyrene–*block*–poly(methyl methacrylate) (PS–PMMA) samples were synthesized by living anionic polymerization. The details of the synthesis are described elsewhere [10–12]. The PS–PMMA weight–average molar masses were from 53,800 to 334,000 g/mol and the PMMA contents were approximately 50% except for two samples where the content was approximately 35% [5,6].

Substituted polyacetylenes were synthesized with $WOCl_4/Ph_4Sn$ or $MoCl_5$ methatesis catalysts in benzene/1,4–dioxane using the standard vacuum break–

seal technique. Before analysis the samples were stored under vacuum.

Characterization Methods

The SEC–MALS measurements were performed at room temperature and at 75 °C using a Hewlett Packard pump series 1100 coupled to a Wyatt Technology Dawn–DSP laser photometer equipped with a He–Ne laser (λ_0=633 nm) and to an Optilab–DSP differential refractometer (DR). The refractive index increments (dn/dc) were measured using an Optilab DSP at λ_0=633 nm. Data acquisition and evaluation were carried out using Astra 4.50 and DNDC 5.00 software. The following columns and eluents were used: (i) a PLgel 5 μm column Mixed D of 30 cm length with a precolumn and the eluents DMF or DMF with added LiBr (0.1 M) at a flow rate of 0.8 mL/min for the association studies of polyurethanes, (ii) a μ–Styragel (10^5) column and 1,4–dioxane/cyclohexane mixtures of different compositions (1.0 mL/min) for micellization studies, and (iii) a series of PLgel columns (10^5Å, 10^3Å and $5{\cdot}10^2$ Å) and THF (1.0 mL/min) for the degradation studies of substituted polyacetylenes.

RESULTS AND DISCUSSION

Association of polyurethanes in N,N–dimethylformamide

Polyurethanes (PU), like some other polar polymers – polyacrylonitrile, acrylic polymers, polyamic acids, show a presence of polydisperse associates in polar amide solvents, which have been ascribed to the formation of polymer complexes with impurities present in DMF [15]. This is in contrast to their dilute solution properties in tetrahydrofuran (THF) and DMF/LiBr, where PU are dissolved molecularly. The intramolecular as well as intermolecular interactions of polymer coils are known to substantially affect the values of the molar mass averages and the distributions determined by the conventional SEC method. The intramolecular associates with compact chain conformations have large elution volumes and, consequently, small relative molar masses; on the other hand, supramolecular structures have small elution volumes and relative molar masses of a few orders of magnitude higher than the actual ones. By using the more advanced SEC–MALS technique it is possible to study the association of polymer chains in solvents and to determine the absolute molar masses and R_g of the associates.

The association behaviour of PU in DMF as a function of composition was investigated using non–carboxylated polyurethanes (H–D0, M–D0, MDI–PTMO) and carboxylated polyurethanes (M–D50). The chemical composition affects the degree of association, which increases with the amount of polar urethane, urea and carboxylic groups in the PU. In the chromatogram of non–carboxylated PUs new small peaks appear at small V_e and are detected by both the DR and LS photometer (Figure 1a). The molar mass of the small peaks is a few orders of magnitude higher than of the main peak (e.g. 10^6 vs. 10^4) and it is more pronounced for carboxylated PU due to the higher amount of polar groups per gram of PU (Figure 1b). A high degree of association of carboxylated PU is also confirmed by a large value of R_g ranging above 100 nm.

The degree of association also increases with decreasing solution concentration (Figure 2) as well as increasing temperature of measurements. After annealing PU solutions at elevated temperatures, the degree of association increases, which is opposite to the usual behaviour of associates. For example, when 0.0002 and 0.0006 g of carboxylated PU M–D50 were injected, the [M_W] were $2.5{\cdot}10^6$ and $5.3{\cdot}10^5$ g/mol; by increasing the temperature from 25°C to 75°C, [M_W] increaseds from $5.3{\cdot}10^5$ to $2.2{\cdot}10^6$ g/mol. A possible explanation for the peculiar behaviour of the polymer solutions in DMF was proposed by Dias and al. indicating that the source of

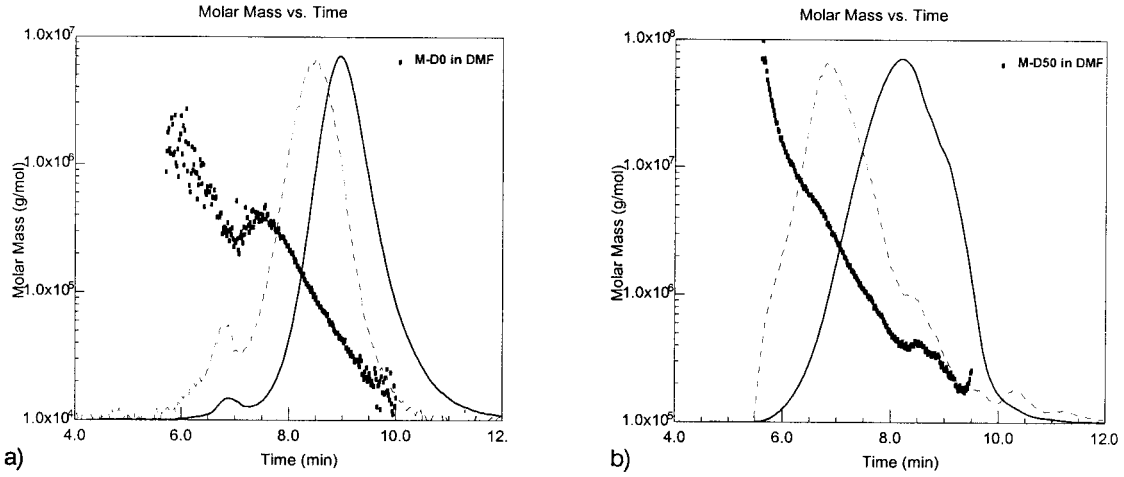

Figure 1. Molar mass as a function of elution time in DMF and the SEC–MALS chromatograms of (a) non–carboxylated polyurethane M–D0, and (b) carboxylated polyurethane M–D50; —— LS response at angle 90°, 3/4 DR response

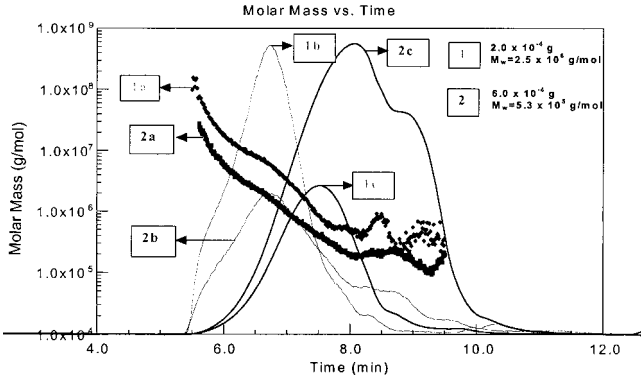

Figure 2. Molar mass as a function of elution time (1a, 2a) and the SEC–MALS chromatograms of carboxylated polyurethane M–D50 in DMF at two injected amounts: (1) 0.0002 g, and (2) 0.0006 g; 3/4 LS response at angle 90° (1b, 2b), 3/4 DR response (1c, 2c)

the intermolecular interaction might be ionic species generated from dissociated diamines and dicarboxylic acids [13]. Indeed, the degree of association drastically increased after the addition of both difunctional degradation products of DMF to the PU solutions, which was also confirmed by NMR spectroscopy. The relationship between all the mentioned parameters and the degree of association demonstrates the important role of impurities present in DMF on the extent of intermolecular interaction in PU solutions [4].

Micellization of block copolymers PS–PMMA

Block copolymer micelles are formed in a selective solvent, *i.e.* a good solvent for one block and precipitant for the other. Micelles are multimolecular copolymer associates with a core formed by a block of low solubility and a protective shell formed by a block of high solubility. The formation of micelles mostly follows the simple closed association model which assumes a dynamic equilibrium between monodisperse micelles and molecularly dissolved copolymer – unimer. Various techniques have been used for the study of micellar systems [14]. The advantages of the size exclusion chromatography (SEC) technique coupled with light scattering were demonstrated to be: the determination of molar mass [10–12] and size (R_g) characteristics of micelles [5, 6], qualitative evaluation of the dynamics of unimer – micelle re–equilibration and the elucidation of the mode of micelle formation (standard closed association or anomalous micellization) [6,12].

We studied the micellar systems of seven PS–PMMA of low polydispersity (M_w/M_n < 1.05) in selective solvents, *i.e.* mixed 1,4–dioxane/cyclohexane (D/C) solvent of different compositions. Micelles with a PMMA core and PS shell were formed at higher contents of cyclohexane (solvent for the PS block and non–solvent for the PMMA block). Due to effective unimer–micelle separation achieved by SEC, it was possible to determine the molar mass averages, gyration radii and their distributions for PS–PMMA micelles by using the SEC–MALS technique. Very narrow molar mass and size distributions of the micelles were typically found (Figure 3a) which is in agreement with the closed association model of micelle formation [5].

For a given copolymer, the association number and molar mass increase significantly as the thermodynamic quality of the solvent decreases. At the same time the increase in R_g is only weak. So, in spite of the high molar masses, the dimensions of the micelles are small. The micellar radius of gyration is predominantly controlled by the copolymer molar mass. In the solvent mixture of a given thermodynamic quality, the association num-

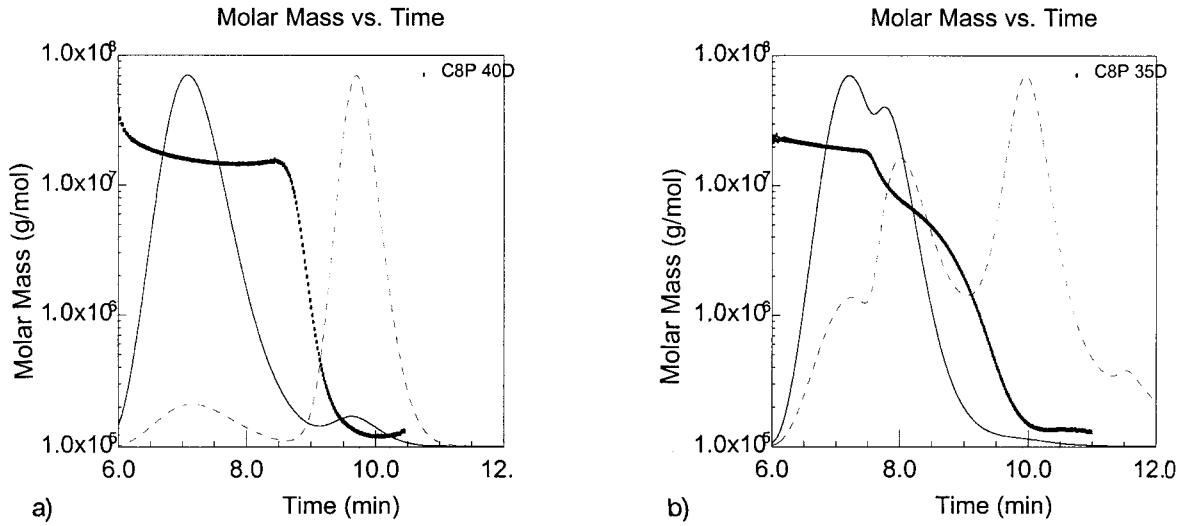

Figure 3. Molar mass as a function of elution time and the SEC–MALS chromatograms of PS–PMMA copolymer (M_w=102,000 g/mol, PMMA content 49.1%) in mixed 1,4–dioxane/cyclohexane solvents: (a) 60 vol% of cyclohexane and (b) 65 vol% of cyclohexane; 3/4 LS response at angle 90°, ––– DR response

ber rises as the length of insoluble PMMA blocks increases and length of soluble PS blocks decreases [5].

For two samples, we also observed the phenomenon of anomalous micellization, showing the simultaneous presence of two kinds of micelles (Figure 3b), *i.e.*, compact regular spherical micelles with lower size and molar mass and anomalous micelles with higher M_w and R_g values. The association number n, M_w and R_g values of these two samples decrease with decreased thermodynamic quality of the solvent from D40/C60 to D35/C65. They also decrease with increasing solution concentration from 5 to 20 mg/mL and the molar mass distributions in some solvent mixtures and solution concentrations show bimodal micellar peaks with higher polydispersity than for unimodal micellar peaks. The first peak with a smaller elution volume and higher M_w and R_g values is ascribed to anomalous micelles, whereas the second peak with a larger elution volume and lower M_w and R_g values represents regular micelles. Their partial separation allowed estimation of the molecular weight and R_g averages of both regular and anomalous micelles [6].

Degradation of substituted polyacetylenes

Stability is a very important factor for the practical use of conjugated polymers in electronic devices. Substituted polyacetylenes are, however, prone to autooxidation in air. They spontaneously slowly degrade in the solid state. The degradation is approx. two orders of magnitude faster in solution, which means that the degradation occuring during polymer analysis can significantly affect the results obtained by classical solution techniques such as static light scattering. The SEC technique, which is very sensitive even to a small extent of degradation proved to be a very suitable technique for such studies [15–17], especially in combination with light scattering detection giving absolute molecular weight averages and distributions. It allows studies of kinetics and mechanisms of polymer degradation [18], as well as estimation of the molar mass of the original, undegraded polymer [15,18].

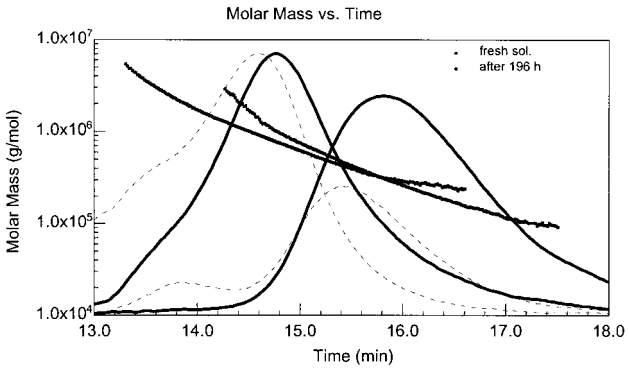

Figure 4. SEC–MALS chromatograms and molar mass as a function of elution time for disubstituted poly(2–hexyne), synthesised with the metathesis catalyst $MoCl_5$: fresh solution (left peak) and after 196h of dissolution (right peak); —— LS response at angle 90°, 3/4 DR response

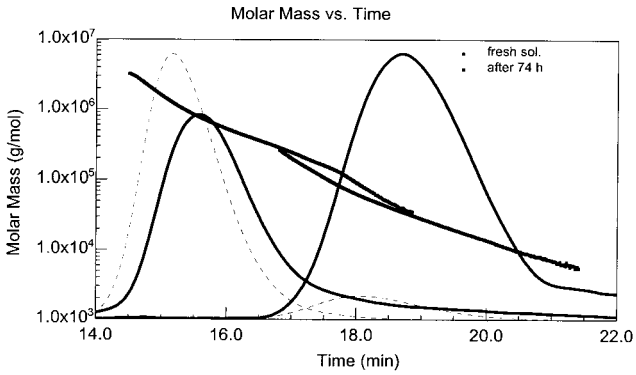

Figure 5. SEC–MALS chromatograms and molar mass as a function of elution time for monosubstituted poly(phenylacetylene), synthesised with the metathesis catalyst $WOCl_4$: fresh solution (left peak) and after 74h of dissolution (right peak); —— LS response at angle 90°, 3/4 DR response

The type of polymerization, as well as the type, position and number of substituents influence the degradation rate and mechanism of degradation of various substituted polyacetylenes. Degradation of the polymers prepared by metathesis polymerization (W– or Mo–based catalysts) is random, whereas of those prepared by insertion polymerisation (Rh–based catalysts) is non–random. The degradation of disubstituted polyacetylenes (Figure 4) is much slower as compared to the degradation of monosubstituted polyacetylenes (Figure 5) due to the steric effects of the two substituents restricting the formation and movement of unpaired electrons (radicals) along the polymer chain.

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IZVOD

KORIŠĆENJE GEL HROMATOGRAFIJE POVEZANE SA RASIPANJEM SVETLOSTI ZA KARAKTERISANJE POLIMERA

(Naučni rad)

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Gel hromatografija povezana sa višeugaonim rasipanjem svetla (SEC–MALS) je korišćena za određivanje molarne mase, radijusa inercije i njihove raspodele za različite tipove polimera. Mi smo koristili SEC–MALS, jednu od najosetljivijih tehnika za detekciju malih udela polimera sa vrlo velikom molarnom masom, za izučavanje: (a) asocijacije poliuretana u N,N–dimetil–formamidu uzimajući u obzir uticaj sastava, koncentracije rastvora i temperature; (b) formiranje micela blok kopolimera u izabranim rastvaračima i, (c) autooksidativnu degradaciju supstituisanih poliacetilena u tetrahidrofuranu.

Ključne reči: Gel hromatografija • Višeugaono rasipanje svetla • Asocijacija poliuretana • Micele blok kopolimera • Degradacija supstituisanih poliacetilena •
Key words: Size exclusion chromatography • Multi–angle light scattering • Association of polyurethanes • Block copolymer micelles • substituted polyacetylene degradation •