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Compositional fractionation of poly(methyl methacrylate)-*graft*-polydimethylsiloxane by reversed-phase high-performance liquid chromatography

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The results are reported of the compositional fractionation of poly(methyl methacrylate)-*graft*-polydimethylsiloxane (PMMA-*graft*-PDMS) by high-performance liquid chromatography (h.p.l.c.) of reversed-phase adsorption mode. Graft copolymers with different compositions were prepared by the radical copolymerization of PDMS macromonomer with MMA, using azobisisobutyronitrile as the initiator in benzene at 60°C. The gradient h.p.l.c. measurements were made using a prepacked column of octyl-modified silica gel, with tetrahydrofuran and acetonitrile as eluents. Detection was performed by an evaporative light-scattering detector. The PMMA-*graft*-PDMS samples were eluted from the components of higher PMMS contents to those of lower PMMA contents, according to reversed-phase adsorption. The present graft copolymers were separated according to their chemical compositions.

(Keywords: compositional fractionation; reversed-phase adsorption h.p.l.c.; graft copolymer)

Introduction

There has been an increasing number of studies on the synthesis of graft copolymers through macromonomers and their applications, since graft copolymers with well defined structures obtained by the macromonomer technique are promising for various applications. However, little attention has been paid to the determination of their chemical heterogeneity. One of the reasons may be that the methods for the determination are limited. So far, only solvent demixing fractionation[1] and high-performance liquid chromatography (h.p.l.c.) based on the adsorption mode[2,3] have given quantitative chemical composition distributions (CCDs) for the graft copolymers.

Stajeskal *et al.*[1] reported the determination of CCD by solvent demixing fractionation of poly(methyl methacrylate)-*graft*-polydimethylsiloxane (PMMA-*graft*-PDMS) prepared from the macromonomer of PDMS. This graft copolymer may be important for industrial applications, since the PDMS macromonomers are commercialized. However, solvent demixing fractionation may not be applied generally to determine CCDs, since it is difficult to find a suitable solvent pair and the method is not established as a rapid and automatic technique. On the other hand, h.p.l.c., which was applied to determine the CCDs of poly(methyl methacrylate)-*graft*-polystyrene (PMMA-*graft*-PS)[2,3], can be applied generally for the present purpose, as a rapid and automatic method.

In the present note, the results are reported of the compositional fractionation of PMMA-*graft*-PDMS, which is the same kind of graft copolymer as that of Stajeskal *et al.*, by h.p.l.c of reversed-phase adsorption mode.

Experimental

The PDMS macromonomer with methacryloyl end-group was supplied by Chisso Co. Ltd. The number-average molecular weight, M_n, corresponding to standard PS estimated by size-exclusion chromatography (s.e.c.) was 1.3×10^4, and M_w/M_n (M_w = weight-average molecular weight) was 1.03. Three samples of the graft copolymer with different compositions were prepared by the radical copolymerization of PDMS macromonomer with MMA using 2,2′-azobisisobutyronitrile (AIBN) as the initiator in benzene at 60°C. The copolymerization mixtures were precipitated with excess methanol. The PMMA-*graft*-PDMS samples were isolated by extracting the respective homopolymers of PDMS and PMMA from the precipitated mixtures with n-hexane and acetonitrile, respectively, using Soxhlet extractors for 24 h.

The PDMS contents of the graft copolymers were determined by 270 MHz ^{1}H n.m.r. spectra (Jeol EX270). The gradient h.p.l.c. instrument was composed of two pumps (Waters, model 510), a controller (Waters, model 680), and a column oven with temperature control system (Waters). A prepacked column of octyl-modified silica gel (TSK-gel Octyl-80Ts, 150 mm × 4.6 mm, particle diameter 5 μm, pore diameter 80 Å) was used. A Varex model Mk II evaporative light-scattering detector was used for detection. The conditions of the detector were as follows: evaporator tube temperature 121.2°C, air pressure 14 psi (9.7×10^4 Pa), attenuation range 2, and recorder range 2 mV. The measurement conditions were as follows: column temperature 30°C, flow rate 1.0 ml min^{-1}, injection volume 100 μl, and sample concentration 0.2 mg ml^{-1}. Tetrahydrofuran (THF) and acetonitrile (ACN), both of which were chromatographic grade from Wako Pure Chemical Co. Ltd, were used as the eluent. The gradient programme of the eluent was as

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Table 1 Synthesis of PMMA-*graft*-PDMS copolymer samples

	Feed				Graft copolymer[a]		
Sample code	Macromonomer (g)	Macromonomer (wt%)	MMA (g)	AIBN (g)	Yield (g)	Conversion (%)	PDMS content (wt%)
A	10.602	68.92	4.780	0.0071	0.297	1.93	49.24
B	7.614	50.05	7.600	0.0121	7.121	46.80	39.59
C	4.799	31.24	10.562	0.0199	9.160	59.63	27.80

Copolymerization conditions: benzene 60 ml, reaction time 96 h at 60°C
[a] Values measured for purified samples of PMMA-*graft*-PDMS

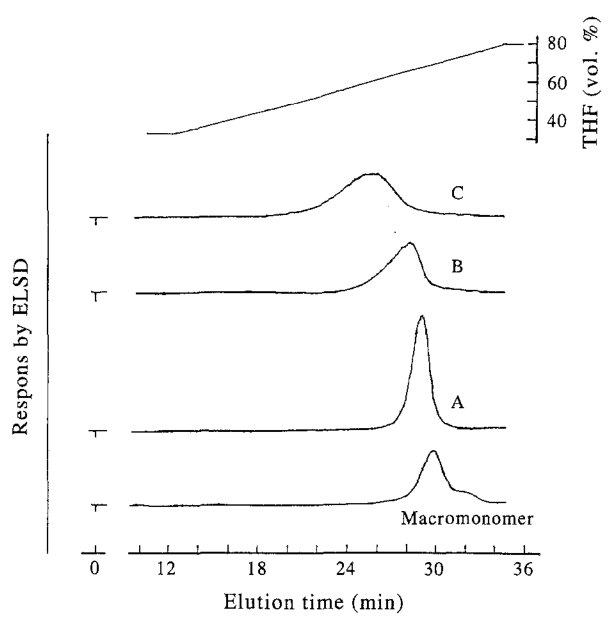

Figure 1 Separation of the PMMA-*graft*-PDMS samples and PDMS macromonomer. Column: TSK-gel Octyl-80Ts, 4.6 × 150 mm, 5 μm, 80 Å. Gradient: acetonitrile/tetrahydrofuran. Detector: Varex model Mk II evaporative light-scattering detector

follows:

Time (min)	0	3	4	34	40	50	60
THF (vol%)	0	0	30	80	100	100	0

Results and discussion

The compositions of the feed and the isolated copolymer are shown in *Table 1*. The macromonomer contents of the graft copolymer samples are smaller than those of the feeds. This result means that the relative reactivity of the macromonomer is lower than that of MMA.

The chromatograms of the PMMA-*graft*-PDMS samples are shown in *Figure 1*. The PMMA-*graft*-PDMS samples were eluted from the components of higher PMMA contents to those of lower PMMA contents, according to the reversed-phase adsorption mechanism[4,5]. That is, PMMA is a polar constituent while PDMS is non-polar in the present copolymer. The present graft copolymers were separated according to their chemical compositions. The chromatograms have to be quantified and converted to CCDs. Quantitative CCDs of PMMA-*graft*-PS determined previously were obtained from the chromatograms detected by the ultraviolet (u.v.) detector. The response of the u.v. detector depends only on the product of the sample concentration and the content of u.v.-sensitive component. However, since the present samples have no u.v. adsorption, an evaporative light-scattering detector (ELSD) was used in the present work. The response of the ELSD varies depending not only on the number of particles but also on the average particle size, the particle size distribution and the refractive index. The number and the size of particles change depending upon the experimental conditions and physical properties of solute and solvents. Therefore, straightforward determination of solute concentration is impossible unless these factors are calibrated for the copolymer compositions[5]. The chromatograms obtained by ELSD cannot be converted to quantitative CCDs, directly.

In the present work the samples of PMMA-*graft*-PDMS were separated according to their chemical compositions by h.p.l.c. of reversed-phase adsorption mode. The study of the quantification of the chromatogram is currently in progress.

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