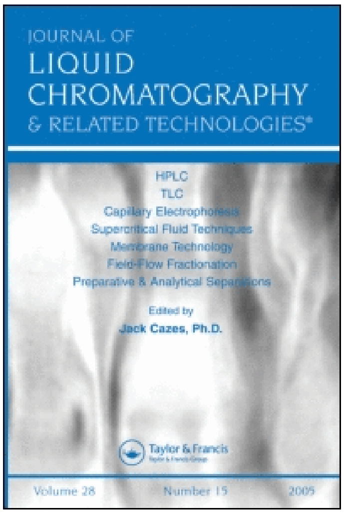

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Styrene-Butyl Methacrylate Copolymers by High Performance Liquid Chromatography

Kenji Ogino[a]; Tooru Maruo[a]; Hisaya Sato[a]
[a] Department of Material Systems Engineering, Faculty of Technology Tokyo University of Agriculture and Technology Koganei, Tokyo, Japan

To cite this Article Ogino, Kenji , Maruo, Tooru and Sato, Hisaya(1994) 'Separation of Styrene-Butyl Methacrylate Copolymers by High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 17: 14, 3025 — 3041

To link to this Article: DOI: 10.1080/10826079408013189

URL: http://dx.doi.org/10.1080/10826079408013189

JOURNAL OF LIQUID CHROMATOGRAPHY, 17(14&15), 3025-3041 (1994)

SEPARATION OF STYRENE-BUTYL METHACRYLATE COPOLYMERS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

KENJI OGINO, TOORU MARUO, AND HISAYA SATO
Department of Material Systems Engineering
Faculty of Technology
Tokyo University of Agriculture and Technology
Koganei, Tokyo 184, Japan

ABSTRACT

Styrene/*n*-butyl methacrylate (S/nBMA) and styrene/*t*-butyl methacrylate (S/tBMA) copolymers were separated by chemical composition using HPLC. In the case of normal phase HPLC using acrylamide gel or acrylonitrile gel as a stationary phase, S/nBMA and S/tBMA copolymers were separated by chemical composition. S/BMA copolymers were eluted from higher styrene content using dichloromethane/*n*-hexane as an eluent, while with the opposite elution order with tetrahydrofuran/iso-octane eluent. The difference of the elution order is explained by hydrogen bondings between the gel and the sample or eluent. In reversed phase HPLC using a styrene column and nonpolar eluent such as dichloromethane/acetonitrile, S/BMA copolymers were eluted from lower styrene content using any kind of eluent examined. On the other hand, an octadecyl methacrylate column provided no separation based on the composition. The separation using the styrene column was ascribed to the specific interaction of the phenyl groups in the sample and the gel. By the comparison of the content of good solvent in an eluent and clouds point of copolymers, it was confirmed that separation was done by adsorption mechanism for both of normal and reversed phase liquid chromatography.

INTRODUCTION

Copolymers usually have chemical composition distribution (CCD) and molecular weight distribution. It is important for the characterization of copolymers to acculately determine CCD, since polymer composition plays an important role in the physical and mechanical properties. Recently, HPLC has been applied to analyze the chemical composition distribution of copolymers[1-30]. It is found that polymers can be separated by the adsorption mechanism either with the combination of polar gel and nonpolar eluent (normal phase: NP) or of nonpolar gel and polar eluent (reverse phase: RP). Thus far, copolymers studied were mainly those consisting of monomers having different polarity, such as, styrene/methyl methacrylate[1-12] or acrylate[13-15], styrene/ethyl (meth)acrylate[16-20], or styrene/acrylonitrile copolymers[21-27].

We reported the separation of several copolymers depending on the chemical composition[4,8,29-31] and polybutadiene depending on the microstructure[32]. In this paper, we studied the separation of S/nBMA and S/tBMA copolymers, which consist of monomers having similar polarity, based on the chemical composition using normal and reversed phase HPLC. Specific interaction of the gel and the sample is discussed.

EXPERIMENT

Samples

Statistical copolymers of styrene-co-*n*-butylmethacrylate (S-nBMA) and of styrene-co-*t*-butylmethacrylate (S-tBMA) were prepared using benzoyl peroxide as an initiator in bulk. The conversion was regulated to be less than 10% in order to obtain samples with a narrow chemical composition distribution. The composition was determined by ^{1}H-NMR measurement. Number and weight average molecular weights, M_n and M_w, respectively, were determined by GPC using a calibration curve for polystyrene. A survey of the samples used is given in TABLE 1 and TABLE 2.

HPLC Columns

Cross-linked acrylonitrile (AN) and octadecyl methacrylate (ODM) gels were prepared by a suspension copolymerization of the monomer and ethylene dimetharylate using 2,2'-azobis(2,4-dimethylvaleronitrile) as an initiator and poly(vinyl alcohol) as a suspensifier. Cross-linked styrene (St gel) was prepared by the smilar suspension copolymerization of styrene and

TABLE 1 Characteristic Data of S/nBMA Coplymers

sample	St unit mole%		Yield		
	in monomer	in polymer	(%)	Mn x 10^{-4}	Mw/Mn
A	84	78	3.7	9.8	1.8
B	70	64	3.8	10.0	1.9
C	55	52	4.5	16.0	2.1
D	29	32	5.3	19.3	1.5
E	14	21	7.4	23.6	1.4

TABLE 2 Characteristic Data of S/tBMA Coplymers

sample	St unit mole% in monomer	St unit mole% in polymer	Yield (%)	Mn x 10^{-4}	Mw/Mn
F	85	72	2.6	7.0	2.1
G	70	57	3.0	7.5	2.0
H	50	46	3.7	7.9	2.0
I	30	26	4.6	8.7	2.0
J	15	13	4.9	15.7	1.4

divinyl benzene. The resulting copolymers were successively washed with hot water, methanol, N,N-dimethylformamide (DMF), and chloroform. Cross-linked acrylamide gel (AA gel) was prepared by an inverse suspension copolymerization of acrylamide and bisacrylamide using 4,4'-azobis(4-cyanopentanoic acid) as a initiator and a mixture of DMF, water, and poly(ethylene glycol) as a diluent, and venton 27 and 34 (NL industries, inc.) as disperse reagents. The resulting copolymer was successively washed with hot water, acetone, DMF, and chloroform. The copolymer beads having diameter of 3-10μm were collected by decantation in acetone. Each gel was packed into a 4.6mm i.d. x 25cm stainless steel column by the slurry method. TABLE 3 shows the survey of HPLC columns.

TABLE 3 Characteristic Data of Packing Materials and Columns for HPLC

Gel	M/D[a)]	Divinyl monomer	Pressure (kg/cm^2)	Flow rate (ml/min.)	Ex.L[b)] ($x10^3$)	NTP[c)]
AA	50/50	BA	200	3.5	6000	2000
AN	67/33	EDMA	450	4.5	500	1800
St	64/36	DVB	300	6.4	500	2000
ODM	50/50	EDMA	90	2.0	500	4000

a):Volume ratio of monomer and divinyl monomer
b):Molecular weight at exclusion limit
c):Number of theoretical plates/25cm
AA, acrylamide; BA, N,N'-methylene-bis(acrylamide); AN, acrylonitrile
EDMA, ethylene dimethacrylate; DVB, divinylbenzene;
ODM, octadecyl methacrylate

HPLC Measurements

HPLC was carried out at room temperature (ca.25°C) using two Jasco 880-PU pumps, one for providing a poor solvent, and the other for a good solvent. The two solvents were mixed together after the pump and were delivered to the injector through a line filter. The flow rate was set at 0.5ml/min and the proportion of good solvent was linearly increased in 25min. A 10μl portion of a dichloromethane solution of the sample (10mg/ml) was injected through a Reodyne 7125 injector. The column effluent was monitored with an ACS (United Kingdom) 750/14 evaporative mass detector.

RESULTS AND DISCUSSION

Separation by Normal Phase HPLC

It has been reported that styrene/methyl methacrylate copolymers can be separated according to the chemical composition by adsorption HPLC. By normal phase (NP) HPLC using a polar gel and a nonpolar eluent, the sample eluted in order of decreasing styrene content, while in the opposite elution order by reversed phase (RP) HPLC, regardless the type of eluent. It is interesting to know the elution behavior of the copolymers consisting of monomers with similar polarities.

A mixture of S-nBMA copolymers with different composition was separated by NP HPLC as shown in FIGURE 1. When a mixture of dichloromethane (DCM)/n-hexane or benzene/n-hexane was used as an eluent with AN or AA column, samples were eluted from higher styrene content. The AA column retarded the elution more than AN column, indicating that the former adsorbed the sample stronger than the latter. On the other hand, when tetrahydrofuran (THF)/iso-octane was used with AA column, samples were eluted from lower styrene content and with poor resolution. With THF/n-hexane or methyl acetate/iso-octane eluent, the same elution order was obtained as with THF/iso-octane eluent.

This is the first example that the elution order of a copolymer is dependent on the type of an eluent. The difference of elution order can be explained by the polarity difference among the sample and by the hydrogen

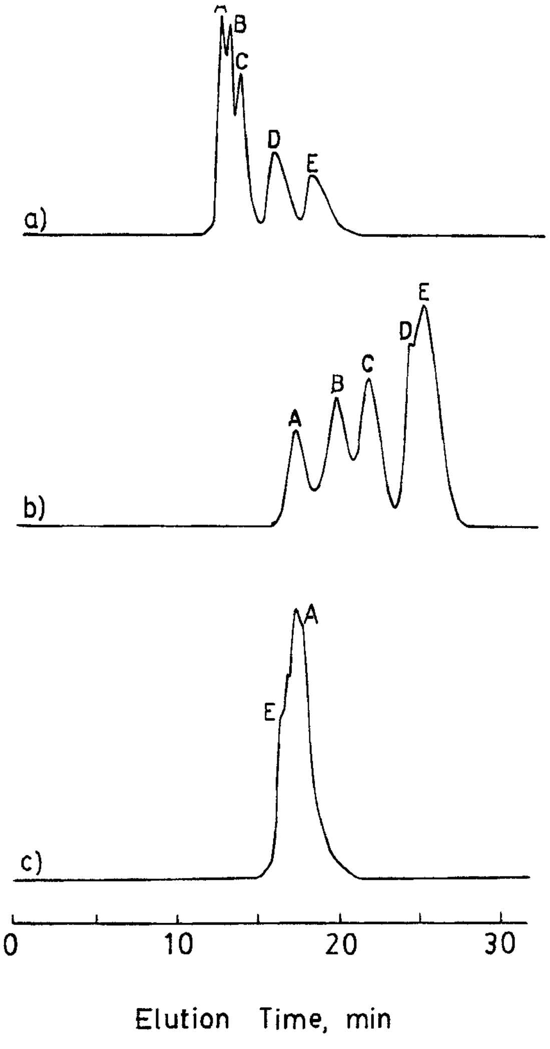

FIGURE 1. Separation of S/nBMA copolymers using (a) AN column and CH_2Cl_2/*n*-hexane eluent, (b) AA column and CH_2Cl_2/*n*-hexane eluent, (c) AA column and THF/iso-octane eluent. The content of CH_2Cl_2 or THF increased from 30 to 80 vol.% in 25 minutes.

bond between the gel and the sample or the eluent. By using DCM or benzene as a component of the eluent, the hydrogen bond was formed between the amide hydrogen in the gel and the carbonyl group in the sample. Since the polarities of both monomer units are similar, copolymer was separated based on the strength of hydrogen bonding with the gel; the sample having higher methacrylate unit eluted later. On the other hand, when oxygen containing solvent was used in the eluent, the hydrogen bond was formed between the gel and the eluent interrupting or reducing the hydrogen bond between the gel and the sample. Therefore, the sample is separated by the difference of the polarity of the sample or by the strength of the interaction between the sample and the eluent.

In FIGURE 2 the content of good solvent (DCM or THF) in the eluent at the peak maximum is plotted against the styrene content together with the cloud point. The content of good solvent is more than 20% higher than the cloud point. Therefore, it is concluded that the separation was governed by adsorption mechanism and not by phase separation one. It is also noteworthy that the cloud point curves have positive slopes for both solvent system indicating that the sample with lower styrene content is more soluble in both eluent. On the other hand, the elution curve for the eluent containing THF has a positive slope, while the slope of the curve for the DCM eluent was negative. Teramachi et al.[28] estimated that the resolution of copolymer would be improved when the slope of elution curve agree with that of cloud point. However, their estimation is not valid in our experiment. It can be concluded that the phase separation, or the solubility does not play signigicant role in the separation using adsorption mechanism.

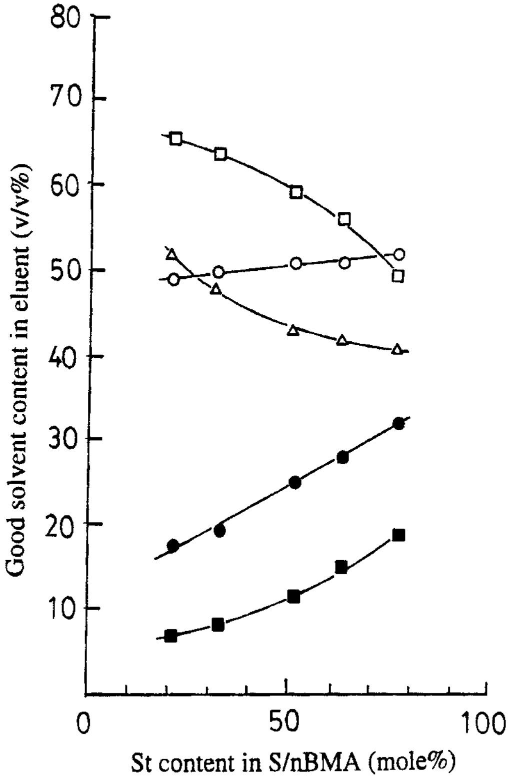

FIGURE 2. Good solvent content of the eluent at peak maximum (open symbols) and cloud point (filled symbol) for S/nBMA copolymers; (open) square: AA column with CH_2Cl_2/*n*-hexane eluent, triangle: AN column with CH_2Cl_2/*n*-hexane eluent, circle: AA column with THF/iso-octane eluent.
(filled) square: CH_2Cl_2/*n*-hexane, and circle: THF/iso-octane.

FIGURE 3 shows the separation of S/tBMA copolymer using AA column. When DCM was used in an eluent, samples with higher styrene content eluted earlier, while opposite elution order was obtained by using THF in an eluent. This elution order is the same as that of S/nBMA.

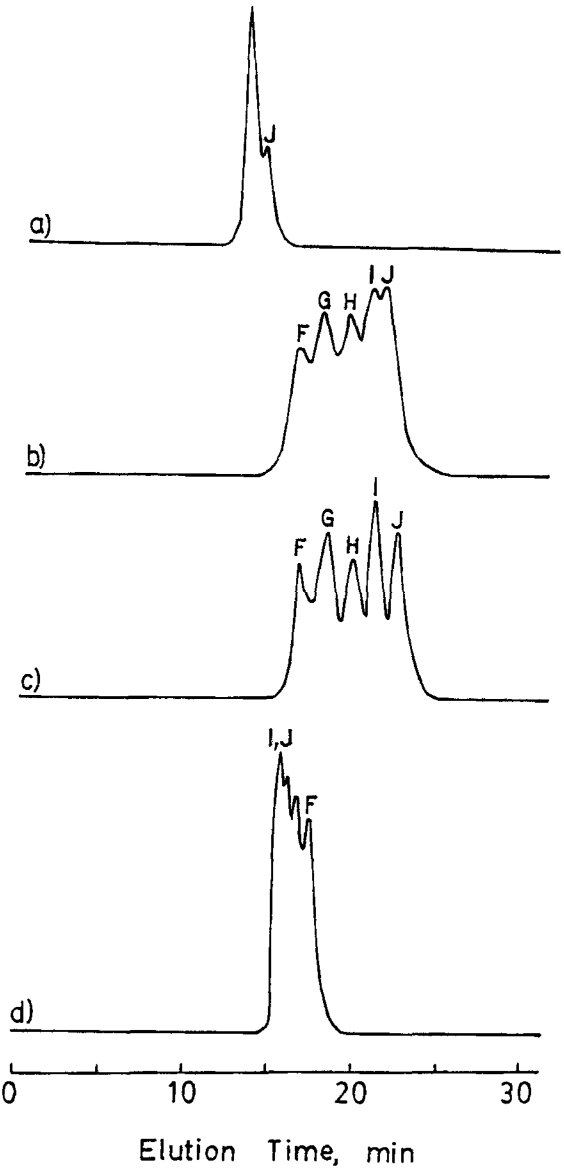

FIGURE 3. Separation of S/tBMA copolymers using (a) AN column and CH_2Cl_2/*n*-hexane eluent, (b) AA column and CH_2Cl_2/*n*-hexane eluent, (c) AA column and CH_2Cl_2/iso-octane eluent, (d) AA column and THF/iso-octane eluent.
The content of CH_2Cl_2 or THF increased from 30 to 80 vol.% in 25 minutes.

Furthermore, the elution volume of S/tBMA was almost the same as that of S/nBMA, if the sample had the same styrene content.

Separation by Reverse Phase HPLC

FIGUREs 4 and 5 show the elution patterns of a mixture of S/nBMA and S/tBMA copolymers, respectively, on the styrene (St) or octadecyl methacrylate (ODM) column using the eluent containing acetonitrile. These systems are reversed-phase (RP) HPLC, since a polar eluent was used with a nonpolar column. When St column was used, the copolymers eluted from the lower St content. This elution order was not changed by the type of good solvent such as THF or benzene. On the other hand, ODM column provided only one peak from a mixture containing 5 copolymers. The elution volumes of S/nBMA and S/tBMA copolymers were almost equal for both columns, when the styrene content was equal. It is noteworthy that the elution volume for ODM column was larger than that for St column, indicating that the sample was adsorbed on the ODM gel stronger than on the St gel.

Glöckner and Müller also found that retention of S/tBMA copolymer increased with styrene content, when THF/iso-octane was used with the phenyl silica column[28]. The elution behavior for the styrene column can be explained by the specific interaction between the phenyl groups of the gel and the copolymer. Thus, the sample was eluted in order of increasing styrene content. On the other hand, ODM column exhibited no specific interaction due to phenyl group providing only one overlapping peak, although it had a stronger hydrophobic interaction between the gel and the sample. Therefore, it can be concluded that the specific interaction such as

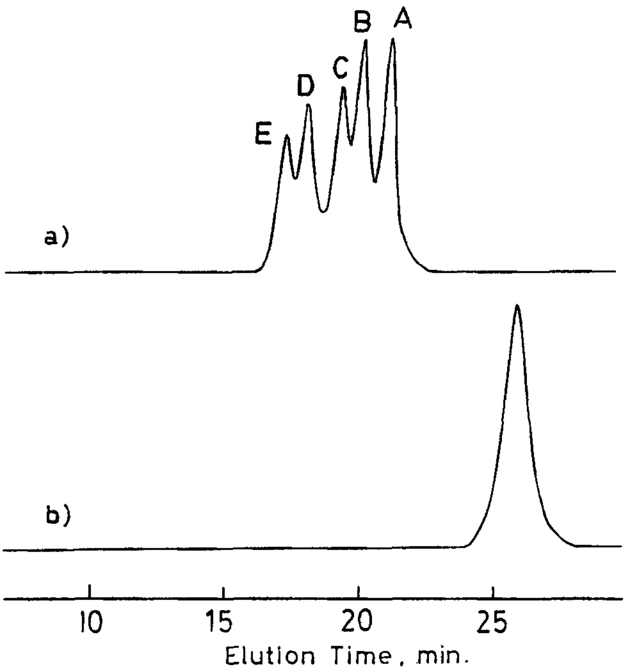

FIGURE 4. Separation of S/nBMA copolymers using (a)St column and (b)ODM column with CH_2Cl_2/CH_3CN (20/80-70/30) eluent.

the hydrogen bonding in NP HPLC or phenyl-phenyl interaction in RP HPLC is necessary to effectively separate the copolymer consisting of monomers with similar polarity.

The content of good solvent (DCM) in the eluent at the peak maximum is plotted against the styrene content together with the cloud point in FIGURE 6. The cloud point curve is lower than the good solvent content curve suggesting that the separation for the RP HPLC was also governed by the adsorption mechanism.

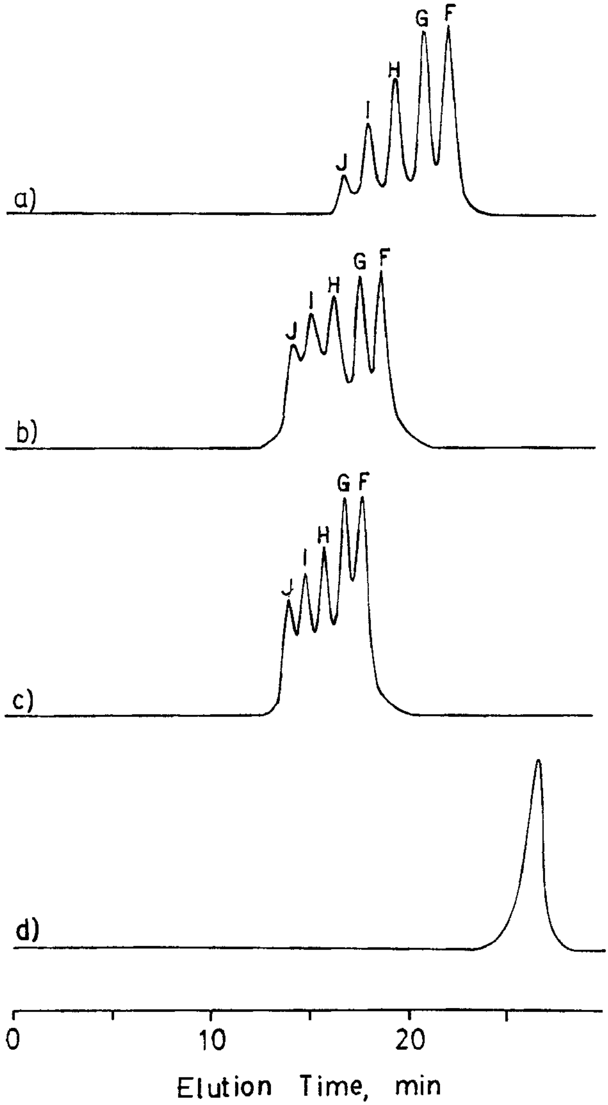

FIGURE 5. Separation of S/tBMA copolymers using St column and (a) CH_2Cl_2/CH_3CN, (b) THF/CH_3CN, and (c) benzene/CH_3CN eluent, and (d) ODM column and CH_2Cl_2/CH_3CN eluent. The content of CH_3CN decreased from 80 to 30 vol.% in 25 minutes.

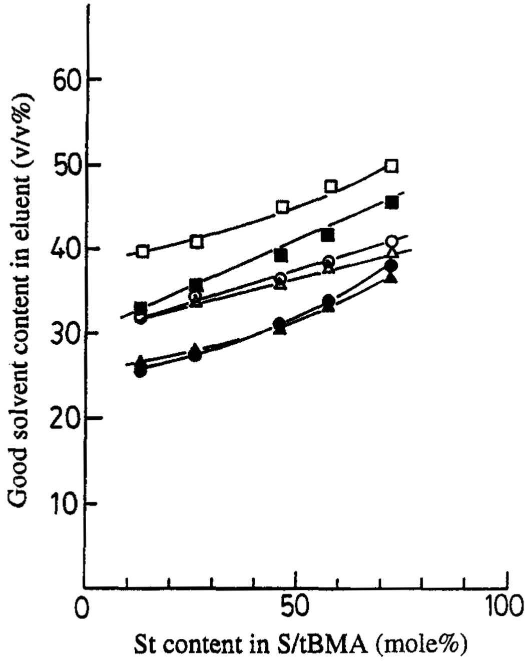

FIGURE 6. Good solvent content of the eluent at peak maximun (open symbols) and cloud point (filled symbols) for S/tBMA copolymers;St column with CH_2Cl_2/CH_3CN (square), THF/CH_3CN(circle) and benzene/CH_3CN(triangle).

The cloud point curve for St/BMA copolymers possessed a positive slope for NP and RP eluents. In the case of St/MMA copolymers, the slope for NP is negative and that for RP is positive when the cloud point is plotted against styrene content[31]. The solubility behavior of St/nBMA and St/tBMA copolymers indicates that the sample with a lower St content is soluble in a wider range of solvents. For example, a copolymer with 20% of St unit is soluble from 6/94 of DCM/n-hexane to 33/67 of DCM/acetonitrile and one with 80% of St unit from 18/82 of DCM/n-hexane to 46/54 of

DMC/acetonitrile. Since the solubility parameter (SP) values of n-hexane, DCM, and acetonitrile are 7.3, 9.6, and 11.8, respectively[33], the former copolymer is soluble in a soluvent with SP value between 7.4 and 11.8, and the latter between 7.7 and 10.8. The SP values of the center of the nonpolar and polar cloud points for the two copolymers are 9.30 and 9.25, which indicates that the St and BMA units has almost the same polarity.

REFERENCES

1) M. Danielewicz and M. Kubin, *J. Appl. Polym. Sci.*, **26**, 951 (1981).

2) G. Glöckner and J. H. M. van den Berg, *J. Chromatogr.*, **352**, 511(1986).

3) S. Mori, Y. Uno, and M. Suzuki, *Anal. Chem.*, **58**, 303 (1986).

4) H. Sato, H. Takeuchi, and Y. Tanaka, *Macromolecules*, **19**, 2613 (1986).

5) S. Mori and Y. Uno, *Anal. Chem.*, **59**, 90(1987).

6) S. Mori and Y. Uno, *J. Appl. Polym. Sci.*, **34**, 2689 (1987).

7) S. Mori, *J. Chromatogr.*, **411**, 355(1987).

8) H. Sato, K. Mitsutani, I. Shinizu, and Y. Tanaka, *J. Chromatogr.*, **447**, 387(1988).

9) S. Mori, *J. Appl. Polym. Sci.*, **38**, 95(1989).

10) S. Teramachi, A. Hasegawa, Y. Shigekuni, and S. Matunaga, *Polymer J.*, **21**, 803 (1989).

11) S. Mori, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **43**, 65 (1989).

12) S. Teramachi, A. Hasegawa, and K. Motoyama, *Polymer J.*, **22**, 489(1990).

13) S. Teramachi, A. Hasagawa, Y. Shima, M. Akatsuka, and M. Nakajima, *Macromolecules*, **12**, 992 (1979).

14) T. H. Mourey, *J. Chromatogr.*, **357**, 101(1986).

15) R. W. Sparidans, H. A. Claessens, G. H. J. van Doremaele, and A. M. van Herk, *J. Chromatogr.*, **508**, 319(1990).

16) S. Mori, and M. Mouri, *Anal. Chem.*, **61**, 2171(1989)

17) G. Glöckner, M. Stickler, and W. Wunderlich, *Fresenius. Z. Anal. Chem.*, **328**, 76 (1987).

18) G. Glöckner, M. Stickler, and W. Wunderlich, *Fresenius. Z. Anal. Chem.*, **330**, 46 (1988).

19) G. Glöckner, *J. Chromatogr.*, **403**, 280(1987).

20) G. Glöckner, H. Kroschwitz, and C. Meissner, *Acta. Polymerica.*, **33**, 614 (1982).

21) G. Glöckner, *Pure. Appl. Chem.*, **55**, 1553 (1983).

22) G. Glöckner, and J. H. M. van den Berg, *Chromatographia*, **19**, 55(1984).

23) G. Glöckner, J. H. M. van den Berg, N. L. Meijerink, T. G. Scholte, and R. Koningsveld, *Macromolecules*, **17**, 962(1984).

24) G. Glöckner, and R. Koningsveld, *Makromol. Chem. Raip Commun.*, **4**, 529 (1983).

25) G. Glöckner, and J. H. M. van den Berg, ,*J. Chromatogr.*, **384**, 135 (1987).

26) G. Glöckner, and J. H. M. van den Berg, *Chromatographia*, **24**, 233 (1987).

27) M. Danielewicz, M. Kubin, and S. Vozka, *J. Appl. Polym. Sci.*, **27**, 3629(1982).

28) G. Glöckner and A. H. E. Müller, *J. Appl. Polym. Sci.*, **38**, 1761 (1989).

29) H. Sato, H. Takeuchi, and Y. Tanaka, *Makromol. Chem. Rapid Commun.*, **5**, 719 (1984).

30) H. Sato, H. Takeuchi, and Y. Tanaka,
International Rubber Conf., Full Text, P. 596(Kyoto, 1985).

31) H. Sato, K. Ogino, S. Maruo, and M. Sasaki,
J. Polym. Sci., Polym. Phys. Ed., **29**, 1073(1991).

32) H. Sato, M. Sasaki, K. Ogino, *Polym. J.*, **23**, 23 (1991).

33) D. L. Saunders, *Chromatography*, 3rd Ed.,
p.96 (1975, Van Nostrand Reinhold, N. Y. Ed., E. Heftmann).

Received: November 5, 1993
Accepted: December 13, 1993