Synthesis of (AB)ₙ-Type Block Copolymers Employing Surface-Active Macro-Azo Initiators

TSUTOMU NAGAMUNE,[1] AKIRA UEDA,[2,*] and SUSUMU NAGAI[1]

[1]Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-81, Japan, and [2]Department of Plastics, Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka, 536, Japan

SYNOPSIS

A macro-azo initiator (MAI), prepared by polycondensation of azobiscyanopentanoyl chloride (ACPC) and polyethyleneglycol having average molecular weight of 1000 (PEG1000), was found to show enough surface activity to be usable as an initiator/surfactant (inisurf). Emulsion polymerization of styrene (St) using this MAI as inisurf was carried out and (AB)ₙ-type poly(PEO-b-PSt) block copolymer (where n represents the block-multiplicity) was obtained. In comparison with solution copolymerization, the emulsion block copolymerization gave PEO-b-PSt with higher molecular weight due to increased block multiplicity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Block copolymers have been synthesized via a radical process initiated by thermal decomposition of azo groups linked with various prepolymers.[1-12] These polymeric azo compounds are called Macro-Azo Initiators (MAIs).[10] Except for the function of initiator, the characteristics of MAIs are almost the same as the prepolymers used. Therefore, MAIs having various functions can be prepared by controlling the characteristics of the prepolymers.

If the prepolymer is hydrophilic and the azo unit is hydrophobic, it is considered that the MAI is a surface-active azo initiator (Inisurf). Several articles have reported on inisurfs previously,[5,13-18] but only few of them treated the synthesis of (AB)ₙ type block copolymers by emulsion copolymerization via inisurfs. In this report, synthesis of a block copolymer of this type with MAI used as inisurf is discussed.

Hydrophilic prepolymers used in this study were polyethyleneglycols (PEGs), having molecular weight of 1000, 2000, and 4000, and 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) was used as a hydrophobic azo compound. Each of the PEGs were

polycondensed with ACPC to prepare MAIs. Here, the MAIs derived from PEGs were named as PEG*s. The asterisk attached represents that the PEG is linked with thermally labile azo units. In the preceding article,[10] (AB)ₙ-type poly(ethyleneglycol)-b-poly(styrene) was synthesized from PEG*s by solution polymerization (Scheme 1). Utilization of PEG*'s surface activity to emulsion polymerization is the aim of the present study.

To evaluate the surface activity of PEG*s, we measured their critical micelle concentration (c.m.c.). Also, a conventional nonionic surfactant, polyethyleneglycol-monododecylether (PEG-de), having average molecular weight of 1200, was used as a control.

Synthesis of (AB)ₙ-type poly(ethyleneoxide)-b-poly(styrene) (PEO-b-PSt) was carried out by emulsion polymerization using a selected PEG* having enough surface activity.
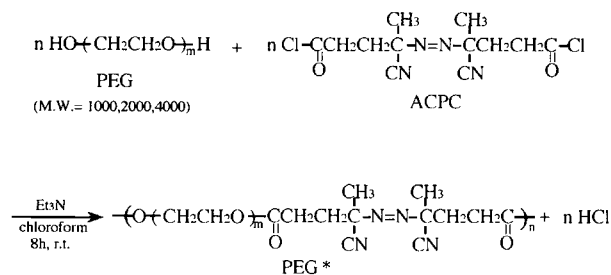
Subsequently, the block copolymers synthesized by solution polymerization were compared with those prepared by emulsion polymerization.

EXPERIMENTAL

Materials

4,4'-Azobis-4-cyanopentanoic acid (ACPA), supplied from Wako Chem. Ind. Ltd., was used without

---

n HO-(CH₂CH₂O-)ₘH   +   n Cl-CCH₂CH₂C-N=N-CCH₂CH₂C-Cl

PEG

(M.W.= 1000,2000,4000)   ACPC

Et₃N
——————→ -(O-(CH₂CH₂O-)ₘ-CCH₂CH₂C-N=N-CCH₂CH₂C-)ₙ + n HCl
chloroform
8h, r.t.

PEG *

Scheme 1 Reaction of PEG with ACPA.

Figure 1 The concentration dependence of surface tension (γ) for PEG*1000 aqueous solution at 293 K. The concentration shown by the arrow corresponds to critical micelle concentration (c.m.c.).

further purification. 4,4'-Azobis-4-cyanopentanoyl chloride (ACPC) was prepared by treating ACPA with PCl_5. Three kinds of extra grade PEG were supplied from Nakalaitesku. Ind. Co. Ltd.: PEG-1000 (av. M.W. = 800, M_w/M_n = 1.08), PEG-2000 (1900, 1.05), PEG-4000 (3440, 1.03), and extra grade PEG-de (1200, 1.09) was from Kanto Chem. Ind. Co. Ltd. They were dried under vacuum for 24 h before use. Commercial styrene was washed with 10% $Na_2S_2O_3$ aqueous solution, 10% NaOH aqueous solution, and distilled water successively, then dried over BaO, and distilled under reduced pressure before use. Commercial, extra pure benzene and chloroform used as solvents were dried over anhydrous Na_2SO_4 just before use. Triethylamine and methanol were used without further purification.

Synthesis of PEG*s

Given amounts of PEG, triethylamine, and chloroform were charged into a four-necked round-bottom flask, equipped with a stirrer, a SiO_2 drying tube, and a dropping funnel charged with a chloroform solution of ACPC. After PEG was dissolved in the solvent at room temperature with stirring, the flask was cooled in an ice bath and the chloroform solution of ACPC was dropped stepwise into the reaction solution. Then the mixture was continuously stirred for 8 h at room temperature to complete polycon-
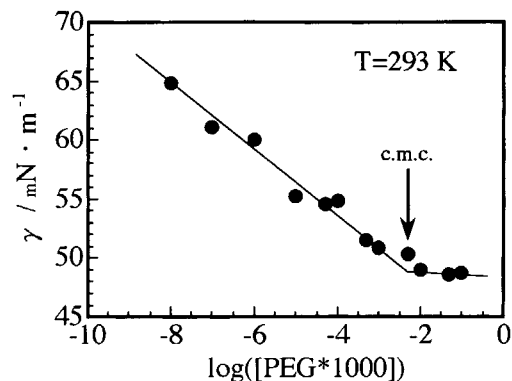
densation. The reaction mixture was poured into a large amount of benzene to precipitate the triethylamine-HCl salt, formed as a by-product, and it was filtered off. PEG* was obtained by evaporating the product solution at 313 K. It was dried under vacuum for more than 24 h before use as an inisurf.

Measurement of the Surface Tension of PEG* and PEG-de Aqueous Solutions

Measurement of the concentration dependence of the surface tension of PEG* and PEG-de solutions to evaluate their c.m.c. was carried out on a Shimadzu surface tensiometer. The instrument was based on the Wilhelmy way. The c.m.c. were determined by plotting the change in the surface tension γ against the concentration of aqueous solution ranging from $10^{-8}M$ to $1.0M$ at 293 K.

Synthesis of PEO-b-PSt by Emulsion Copolymerization

Given amounts of PEG*, styrene, and distilled water were charged into a reaction vessel with a stirrer so

Table I The Results of Polycondensation

	Feed					Products		
	PEG		ACPC	TEA	CHCl₃	Yield	Conversion	Molecular Weight
Run No.		g	g	g	mL	g	%	Mpᵃ
1	PEG1000	5.05	1.60	1.02	100	6.18	98.4	11200, 800
2	PEG2000	5.16	0.82	0.52	100	5.66	97.9	7800, 5010, 2100
3	PEG4000	4.03	0.32	0.20	100	4.03	94.3	10900, 7900, 3700

ᵃ Mp indicates the value of molecular weight at peaks of GPC curve.

Table II The Critical Micelle Concentration (c.m.c.) and Surface Tension

Sample	c.m.c./mol · L^{-1}	$\gamma_{C.M.C.}$/mN · m^{-1}
PEG-de	1.24*10^{-5}	40.3
PEG*1000	6.67*10^{-3}	48.9
PEG*2000	—	—
PEG*4000	—	—

In case of PEG*2000 and PEG*4000, micelle was not formed.

that the reaction mixture volume was 50 mL, and the reaction mixture was kept with stirring for 0.5 h to get uniform dispersion of styrene. Polymerization was performed for 5 h at 338 K, with stirring (400 r.p.m.). After polymerization, the vessel was cooled by an ice bath, and the mixture was poured into a large amount of methanol to precipitate the product. Then the product was filtered off and washed thoroughly with methanol to remove nonreacted PEG* from the product. Block copolymer thus obtained was dried under vacuum for more than 48 h.

Synthesis of PEO-*b*-PSt by Solution Polymerization

A glass tube was charged with given amounts of PEG*, styrene, and benzene, and was sealed after

degassing with freeze thawing, and then the tube was kept at 338 K in an oscillating water bath for 5 h. After that, the tube was cooled by an ice bath to terminate the polymerization. The reaction mixture was poured into a large amount of methanol to collect the product as a precipitate. The product was filtered off and washed thoroughly with methanol, and then was dried under vacuum for more than 48 h.

Characterization of Block Copolymers

GPC measurements were carried out on a Gilson HPLC system model 302–303 microflow mode, with Gilson Refractive Index Detecter132 and a Tosoh GMH$_{HR}$-M column. The conditions were as follows: solvent, tetrahydrofuran (THF); flow rate, 0.5 mL/min.; column temperature, 313 K. The molecular weight was calibrated with polystyrene standard (from Pressure Chem. Co.). ^{1}H-NMR spectra of products were taken on a Hitachi R-600 spectrometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of PEG*

Table I shows the results of the preparations and GPC measurements of PEG*s. The rather high

Table III The Results of Emulsion Copolymerization with PEG*1000

	Feed			Copolymer	
	PEG*1000	St Monomer	Water	Yield	St Conversion
Run No.	g	g	g	g	%
1	5.02 (4.04)	5.05	40.0	5.43	69.6
2	3.01 (2.42)	5.02	42.0	3.23	59.5
3	2.50 (2.01)	5.02	42.5	3.72	66.2
4	2.01 (1.62)	5.03	43.0	3.16	68.0
5	1.51 (1.21)	5.01	43.6	2.62	44.7
6	1.05 (0.840)	5.01	44.1	2.09	40.8
7	0.50 (0.402)	5.04	44.5	0.680	17.2
8	1.01 (0.810)	1.03	48.0	0.366	50.9
9	1.00 (0.804)	2.03	47.0	0.626	19.1
10	1.01 (0.812)	4.03	45.0	1.10	30.2
11	1.05 (0.840)	5.01	44.1	2.09	40.8
12	1.02 (0.822)	6.00	43.3	1.44	25.0
13	1.02 (0.818)	7.02	42.0	3.20	45.4
14	1.01 (0.808)	8.01	41.1	1.39	17.4
15	1.00 (0.806)	10.0	39.3	1.90	18.9

Reaction condition was 338 K, 5 h stirring and total volume was 50 mL. The number in ( ) denotes weight of EO component in PEG*1000.

Table IV   The Results of Solution Copolymerization with PEG*1000

| | Feed | | | Copolymer | |
| | PEG*1000 | St Monomer | Benzene | Yield | St Conversion |
Run No.	g	g	g	g	%
1	0.513 (0.412)	0.520	3.91	0.123	17.8
2	0.423 (0.300)	0.510	3.92	0.117	23.3
3	0.299 (0.294)	0.515	3.92	0.122	20.5
4	0.199 (0.160)	0.506	3.91	0.108	18.6
5	0.103 (0.0828)	0.505	3.90	0.0894	18.3
6	0.0560 (0.0450)	0.516	3.90	0.0712	13.4
7	0.105 (0.0844)	0.407	4.00	0.0635	14.8
8	0.103 (0.0828)	0.505	3.90	0.0844	18.3
9	0.101 (0.0812)	0.615	3.83	0.166	25.7
10	0.108 (0.0868)	0.831	3.62	0.109	11.4

Reaction condition was 338 K, 5 h stirring and total volume was 5 mL. The number in () denotes weight of EO component in PEG*1000.

yields might suggest the inclusion of unreacted materials. The molecular weights of PEG*s obtained were at most around 10,000. Polycondensation started with PEG1000, having the lowest molecular weight among PEGs used, resulted in the highest degree of polycondensation. From the view point of block efficiency of MAI, such higher degree of polycondensation is more desirable.

Figure 1 shows the concentration dependence of γ for PEG*1000 aqueous solutions. Value of γ

Table V   Composition and Molecular Weight of Copolymers by Emulsion Copolymerization

| | Fraction Ratio in Feed | Copolymer | | | | |
| | | EO Fraction | St Fraction | Molecular Weight | | |
Run No.	[EO]/[St]	Wt %	Wt %	Mp[a]	$\bar{M}_n$	$\bar{M}_w$
1	0.799	9.12	89.0	49500	27500	72000
2	0.482	8.91	89.2	61000	36000	91000
3	0.400	9.07	89.0	61000	34000	91000
4	0.321	8.40	89.8	62000	39000	79000
5	0.242	6.75	91.8	55000	32000	65000
6	0.168	3.64	95.6	75000	39000	94000
7	0.0797	3.53	95.7	75000	28000	82000
8	0.788	8.10	90.2	31000	19000	45000
9	0.396	9.74	88.2	58000	18000	57000
10	0.201	5.39	93.5	63000	29000	64000
11	0.168	3.64	95.6	75000	39000	79000
12	0.131	4.73	94.3	69000	35000	75000
13	0.117	4.00	95.2	60000	33000	63000
14	0.101	4.45	94.6	99000	46000	101000
15	0.0805	3.32	96.0	83000	40000	87000

[a] Mp indicates the molecular weight at peaks of GPC curve.

reduced with increasing PEG*1000 concentration, and then kept constant passing over the point of c.m.c. indicated by an arrow, where the surfactant occupies the water–air interface completely and begins to form micelles. Table II summarizes the results of c.m.c. and $\gamma_{c.m.c.}$ measurements. For PEG-de and PEG*1000, c.m.c. were observed within the range of the concentration, while for PEG*2000 and PEG*4000, c.m.c. were not found. Therefore, only PEG*1000 among the three kinds of PEG* could be used as an inisurf. However, because PEG*1000 showed considerably higher c.m.c. than PEG-de, the surface activity of PEG*1000 seemed to be not so strong. The $\gamma_{c.m.c.}$ of PEG-de was 40.3 mN/m, while that of PEG*1000 was 48.9 mN/m. It is considered that the hydrophobicity of PEG*1000 is not strong, resulting in higher c.m.c. Further, in the case of other PEG*s, a smaller ratio of hydrophobic moiety to hydrophilic one might be responsible for the absence of c.m.c..

Synthesis and Characterization of PEO-b-PSt

Among PEG*s prepared, only PEG*1000 was submitted for surface active MAI to synthesize block copolymers. Table III summarizes the results of synthesis of block copolymers by emulsion polymerization, and Table IV summarizes those of solution polymerization. Each polymerization was carried out under the same conditions such as feed
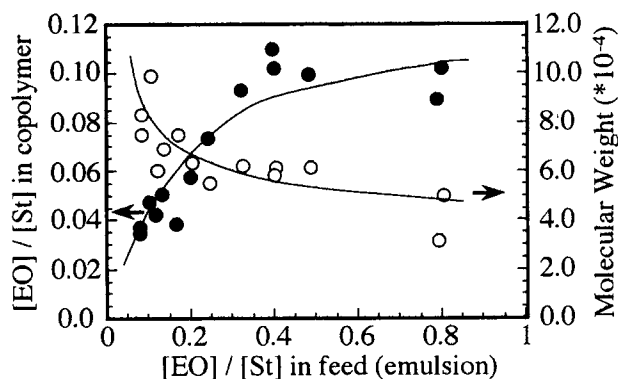

Figure 2 The relationship of copolymer composition ratio (●) and M.W. (○) vs. feed composition ratio obtained by emulsion copolymerization for 5 h at 338 K.

ratio and temperature to compare with each other. The St conversion in Tables III and IV were calculated as follows:

St conversion (%)

$$= \frac{\text{(wt. of product and recovered PEG*)} - \text{(Fed wt of PEG*)}}{\text{(Fed wt of St monomer)}} \times 100$$

The yields and conversions varied with the feed ratio of PEG*1000 and St, but on the whole, emulsion polymerization gave higher ones in comparison with solution polymerization.

Table VI   Composition and Molecular Weight of Copolymers by Solution Copolymerization

Run No.	Fraction Ratio in Feed [EO]/[St]	Copolymer				
		EO Fraction Wt %	St Fraction Wt %	Molecular Weight		
				Mp^a	$\bar{M}_n$	$\bar{M}_w$
1	0.793	6.90	91.7	5700	4700	6100
2	0.599	6.95	91.6	5200	4700	6100
3	0.459	5.15	93.8	6100	5400	6900
4	0.316	4.35	94.7	7200	6200	8000
5	0.164	4.04	95.1	10100	8000	10400
6	0.0872	4.02	95.1	16000	12200	16700
7	0.207	4.78	94.2	5300	4800	5900
8	0.164	4.04	95.1	8000	7100	9200
9	0.132	4.03	95.1	12700	9800	13000
10	0.104	3.91	95.3	16500	12200	16600

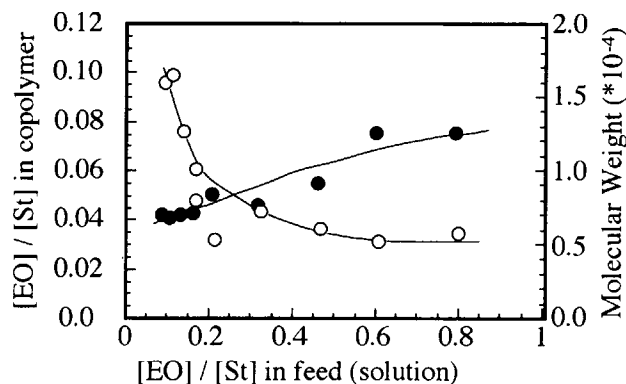^{a} Mp indicates the molecular weight at peaks of GPC curve.

Figure 3 The relationship of copolymer composition ratio (●) and M.W. (○) vs. feed composition ratio obtained by solution copolymerization for 5 h at 338 K.

Tables V and VI summarize the results of GPC measurements and the compositions of block copolymers [ethylene oxide (EO) and styrene (St)] from ^{1}H-NMR spectra for the series of runs shown in Tables III and IV. Figures 2 and 3, respectively, shows the copolymer composition ratio (EO/St) and molecular weight vs. the composition in feed ([EO]/[St]) plotting the data of Tables V and VI. The molecular weight of copolymer increased with the decrease in the feed ratio of [EO]/[St], which is reasonable from the view point of radical initiation by PEG*1000. As for the composition of block copolymer, only a very small fraction of EO could be incorporated in the copolymer even if the feed ratio of [EO]/[St] was increased up to 0.8. Emulsion system gave the copolymer containing a little higher, or around the same order of, EO fraction in comparison with solution system, however, the molecular weight of the emulsion copolymer was several ∼ 10 times higher than that of solution copolymer.

In ordinary emulsion polymerization, a primary radical of an initiator enters into a micelle from the aqueous phase and initiates the polymerization. Termination occurs only after another radical comes inside the micelle to meet the propagating radical, and, thus, a longer polymer chain is formed in comparison with other polymerization systems such as solution, bulk, and suspension. In the case of using inisurf, however, a pair of radicals occur at the same time in one micelle and extraordinarily longer growth of polymer chain is not expected because the chance of termination between the propagating radicals exists similarly to the case of other polymerization systems. Here, for the case of using macro-inisurf containing PEG, both terminals of the PEG* chain take a role of initiation

of St polymerization, while PSt radicals terminate by recombining each other. Therefore, increased molecular weight of product in this system must be the result of an increased degree of block multiplicity of a copolymer.

The fact that the copolymer composition ratio (EO/PSt) of the emulsion system was a little higher, but around the same order, in comparison with the case of solution polymerization, in contrast to the significant difference in molecular weight, supports the above discussion. The reason for occurring the block multiplicity more increased in emulsion system is not clear, but it is considered that a close aggregation like a micelle of PEG* segments should have helped to recombine with each other to form a larger block copolymer.

CONCLUSION

Three kinds of PEG*s 1000, 2000, and 4000, from which (AB)$_n$ type block copolymers were expected to be derived, were prepared and evaluated for using as inisurf. But PEG*1000 only could be used as inisurf. The value of c.m.c. of PEG*1000 was higher than that of PEG-de, a commercial nonionic surfactant, because the hydrophobicity of PEG*1000 was not strong. However, PEO-b-PSt block copolymers of (AB)$_n$ multiblock type could be synthesized by emulsion polymerization with PEG*1000 as inisurf. Comparing the products of emulsion polymerization with those of solution polymerization under the same conditions, much increased block multiplied (AB)$_n$-type block copolymers with higher molecular weight were obtained than those of solution polymerization.

REFERENCES

1. A. Ueda, Y. Shiozu, and S. Nagai, *Polym. Prep. Jpn.*, **21**, 343 (1972).
2. M. H. George and J. R. Ward, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 2909 (1973).
3. A. Ueda, Y. Hidaka, and S. Nagai, *Polym. Prep. Jpn.*, **22**, 348 (1973).
4. J. J. Laverty and Z. G. Gardlund, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2001 (1977).
5. R. Walz, B. Bömar, and W. Heitz, *Makromol. Chem.*, **178**, 2527 (1977).
6. R. Walz and W. Heitz, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1807 (1978).
7. A. Ueda, K. Hiramatsu, and S. Nagai, *Polym. Prep. Jpn.*, **32**, 304 (1983).

8. A. Ueda, and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1611 (1984).

9. A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1783 (1984).

10. A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 405 (1986).

11. B. Hazer et. al., *Makromol. Chem.*, **190**, 1987 (1989).

12. A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1721 (1990).

13. H. R. Dicke and W. Heitz, *Makromol. Chem. Rapid Commun.*, **2**, 83 (1981).

14. H. R. Dicke and W. Heitz, *Colloid Polym. Sci.*, **260**, 3 (1982).

15. K. Tauer et. al., *Makromol. Chem. Macro. Symp.*, **31**, 107 (1990).

16. K. Tauer, A. Wedeo, and E. M. Morozova, *Makromol. Chem.*, **193**, 1387 (1992).

17. I. M. H. Kusters et. al., *Macromolecules*, **25**, 7043 (1992).

18. A. Guyot and K. Tauer, *Adv. Polym. Sci.*, **111**, 43 (1994).