

The Influence of Hydrophilic and Hydrophobic Domains on Water Wettability of 2-Hydroxyethyl Methacrylate-Styrene Copolymers

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Synopsis

Cooligomers and ABA-type block copolymers composed of a hydrophilic monomer, 2-hydroxyethyl methacrylate (HEMA), and a hydrophobic monomer, styrene, were synthesized to study the relation between their microstructure and hydrophilic and hydrophobic functions. Films of cooligomers and ABA-type block copolymers were cast from DMF solutions at 40°C. The wettability, which was determined from the contact angle with water, increased considerably when HEMA mole fraction reached around 0.8 in the cooligomer system and around 0.9 in the ABA-type block copolymer system. The microstructures of the copolymer films were observed by electron microscopy using the osmium tetroxide fixation technique. The morphologic change in the domain structure was observed at an HEMA mole fraction of about 0.8 in the cooligomer system and about 0.9 in the ABA-type block copolymer system. It is suggested that hydrophilic and hydrophobic functions are largely influenced by the state of aggregation of each segment, that is, the size and geometry of the hydrophilic and hydrophobic domains.

INTRODUCTION

Poly(2-hydroxyethyl methacrylate) (poly-HEMA) exhibits amphiphilic properties, because the backbone of polymer chains and the α -methyl group are hydrophobic and the hydroxyethyl group is hydrophilic. The poly-HEMA gel, which is a biocompatible material,¹ is used as contact lenses, coating of surgical suture, material,² etc.

Many studies³ on the syntheses and the properties of poly-HEMA have been reported. However, most of these studies were concerned with crosslinked poly-HEMA, and little was reported on linear poly-HEMA and its copolymers because gelation often occurred when HEMA was polymerized.

We have studied the copolymerization and cooligomerization of a hydrophilic monomer, HEMA, with a hydrophobic monomer, styrene (St), to investigate the syntheses and the properties of the linear amphiphilic polymer.^{4,5} The cooligomers and the block copolymers of HEMA and St are good models for studying the influence of the state of aggregation of each segment on the properties of the copolymer. In this paper, syntheses of semitelechelic oligo-HEMA and HEMA-St ABA-type block copolymer were performed to study the relation between their microstructure and the wettability by water. The microstructure of the films of the random cooligomer and the ABA-type block copolymer was observed by electron microscopy using the osmium tetroxide fixation technique. It is proposed that the wettability with water is influenced by the hydrophilic and the hydrophobic domains of HEMA-St random cooligomer and ABA type block copolymer.

EXPERIMENTAL

Purification of Materials

α,α' -Azobisisobutyronitrile (AIBN), *n*-butanethiol (*n*-BuSH), 2-aminoethanethiol (AESH), and St were purified by conventional methods. HEMA was distilled under reduced pressure of nitrogen, and the fraction of bp 87°C/5 mm Hg was used. N,N-Dimethylformamide (DMF) was distilled under reduced pressure after drying over anhydrous magnesium sulfate. Tetrahydrofuran (THF) was distilled after drying over anhydrous magnesium sulfate. Methanol was distilled at first and then redistilled after refluxing in the presence of magnesium and small amounts of iodide.

Cooligomerization

A methanol solution containing the desired amounts of AIBN, HEMA, St, and *n*-BuSH was taken into an ampoule. The ampoule was immersed in liquid nitrogen and evacuated to less than 10^{-5} mm Hg. The ampoule was then isolated from the system and allowed to warm sufficiently to melt the content. The liquid was refrozen in liquid nitrogen, and the degassing operation was repeated. Finally, the ampoule was sealed at less than 10^{-5} mm Hg. The sealed ampoules were shaken vigorously and immersed in an oil bath held at $60.0^\circ \pm 0.1^\circ\text{C}$. After the proper reaction time, the ampoules were removed from the bath and immediately frozen in liquid nitrogen. They were then warmed sufficiently to melt and the contents were poured into an ether-petroleum ether mixed solvent to precipitate the cooligomers. The precipitated cooligomers were collected on a tared sintered-glass filter and washed thoroughly with the precipitant mixture. The samples were dried in a vacuum desiccator.

Synthesis of HEMA-St ABA-Type Block Copolymer

Synthesis of Amino-Semitelechelic Oligo-HEMA

A DMF solution containing the desired amounts of AIBN, HEMA, and AESH as chain transfer agent was weighed into an ampoule. The ampoules were sealed by conventional methods and immersed in an oil bath held at $60.0^\circ \pm 0.1^\circ\text{C}$ for a given period of time. The contents were then poured into ether to precipitate the oligomers. The oligomers were collected on a tared sintered-glass filter and dried in a vacuum desiccator.

Synthesis of Isocyanate-Telechelic Oligo-St

Preparation of *p,p'*-Diisocyanate Diphenyl Disulfide (IPDS). *p*-Chloronitrobenzene was reacted with sodium sulfide to synthesize *p*-aminobenzenesodium thiolate. It was oxidized by hydrogen peroxide to synthesize *p,p'*-diamino diphenyl disulfide⁶ (APDS). Hydrogen chloride was added to the methanol solution of APDS to prepare its salt. After drying, phosgene-carbon tetrachloride solution was gradually added dropwise to the *o*-dichlorobenzene suspension of APDS salt held at 100°–110°C and allowed to react with stirring for 8 hr. Then, after evaporating the carbon tetrachloride, the residue was

reacted at 140°–150°C for 5 hr. After cooling, insoluble materials were filtered out and the gaseous component and the solvent were evaporated under reduced pressure. The obtained samples were recrystallized twice in *n*-hexane.

Photopolymerization of St. The desired amounts of St and IPDS were weighed into quartz ampoules which were sealed in the usual way. Stirred in a water bath at 30°C, the ampoules were irradiated with the ultraviolet light (Toshiba SHL 100 UV) for a given number of hours at a distance of 15 cm. The polymerized contents were diluted with benzene and poured into *n*-hexane to precipitate the isocyanate-telechelic oligo-St. The obtained oligomers were dried in a vacuum desiccator.

ABA-Type Block Copolymerization

Under the condition of $[\text{NH}_2]/[\text{NCO}] = 1.2$, amino-semitelechelic oligo-HEMA (prepolymer A) and isocyanate-telechelic oligo-St (prepolymer B) were allowed to react with stirring in DMF solvent at 0°C for 24 hr. The reactants were poured into ether. The precipitated sample was filtered and dried in a vacuum desiccator. The DMF solution of the obtained sample was then poured into methanol-isopropyl alcohol mixed solvent. The purified copolymer was filtered out and dried in a vacuum desiccator.

Analysis of Oligomers and Copolymers

The structure of the polymers was confirmed by infrared spectroscopy (Hitachi EFI G-III Type). Number-average molecular weight (M_n) of oligo-HEMA was determined by vapor pressure osmometry (Hitachi V.P.O. 117 Type) in methanol solvent. The intrinsic viscosity of oligo-St was measured with an Ubbelohde viscometer in benzene at $25^\circ \pm 0.05^\circ\text{C}$, and its molecular weight was determined from the viscosity equation.⁷ Amino group concentration was determined by the titration of acetic acid solution of amino-semitelechelic oligo-HEMA with 0.02*N* perchloric acid-acetic acid solution using crystal violet as an initiator.⁸ Isocyanate group concentration was determined by back-titration with 0.1*N* HCl-methanol solution using bromophenol blue as initiator, after the reaction of a given concentration *n*-dibutylamine-chlorobenzene solution with isocyanate-telechelic oligo-St for 48 hr at room temperature.⁹

Measurement of Wettability

DMF solutions containing about 10 wt % of the polymers were prepared. Films were cast from these solutions on clean microscope glass slides, evaporating the solvent slowly in an oven at 40°C for one day. After drying under reduced pressure, the advancing contact angle exhibited by a sessile drop of water on the polymer surface was measured after 10 sec by a contact angle goniometer (Erma goniometer G-I Type). The contact angles were measured at various points of ten film samples (2.4 cm × 5 cm).

The contact angle of the drop of water was constant for about 1 min after water was dropped, but was found to decrease about 1°–3° after 2 min and about 3°–5° after 3 min because the water was absorbed by the polymer. Therefore, wettability was measured under conditions not influenced by water absorption of the polymer.

TABLE I
 HEMA-St Cooligomerization^a

HEMA mole fraction in monomer	Time, min	Conversion, %	HEMA mole fraction in cooligomer	Cooligomerization rate $R_p \times 10^5$, mol/l.-sec
0.2	90	1.97	0.469	1.29
0.3	90	4.02	0.585	2.24
0.4	90	5.68	0.680	3.73
0.5	60	6.69	0.765	6.61
0.6	60	9.69	0.808	9.63
0.8	40	7.40	0.846	11.5
0.9	30	5.05	0.890	10.6

^a [AIBN] = 5×10^{-3} mol/l.; [M] = 3.7 mol/l.; [S]/([M₁] + [M₂]) = 0.020.

Electron-Microscopic Observation

DMF solutions of the polymer were made to flow on carbon-coated copper grid and thin films were prepared by evaporating at 40°C. After drying under reduced pressure, the films were fixed by osmium tetroxide vapor for 6 hr. The microstructures were observed by an electron microscope (Hitachi HU-11 Type).

RESULTS AND DISCUSSION

Oligomerization

In the case of polymerization of HEMA, gelation occurred at a conversion of beyond 20–30%. The linear poly-HEMA, however, could be prepared by solution polymerization used with a suitable chain transfer agent. Thiol compounds were suitable chain transfer agents to control the molecular weight of oligo-HEMA. The HEMA-St cooligomerization with small amounts of thiol compounds could

 TABLE II
 Preparation and Analysis of Prepolymer

Prepolymer no. ^a	[S]/[M]	Time, hr	Conversion, %	Molecular weight from analysis of endgroup	M_n	Number of NH ₂ or NCO groups in one molecule
A-1	0.085	3	28.72	10,000	10,400 ^a	1.04
A-2	0.250	3	20.60	3,850	3,780 ^b	0.98
B-1	0.010	8	16.50	13,300	12,300 ^c	1.85
B-2	0.025	11	25.10	10,300	10,500 ^c	2.04
B-3	0.050	8	19.40	5,500	5,500 ^c	2.02
B-4	0.100	23	29.80	2,100	2,100 ^c	2.00

^a A: Oligo-HEMA, in DMF (2.5 mol/l.) at 60°C. B: Oligo-St B-1, 2, and 3, bulk system; B-4, in THF (4 mol/l.) at 30°C.

^b V.P.O. in MeOH at 40°C.

^c $[\eta] = (3.64 \times 10^{-4}) M^{0.64}$.

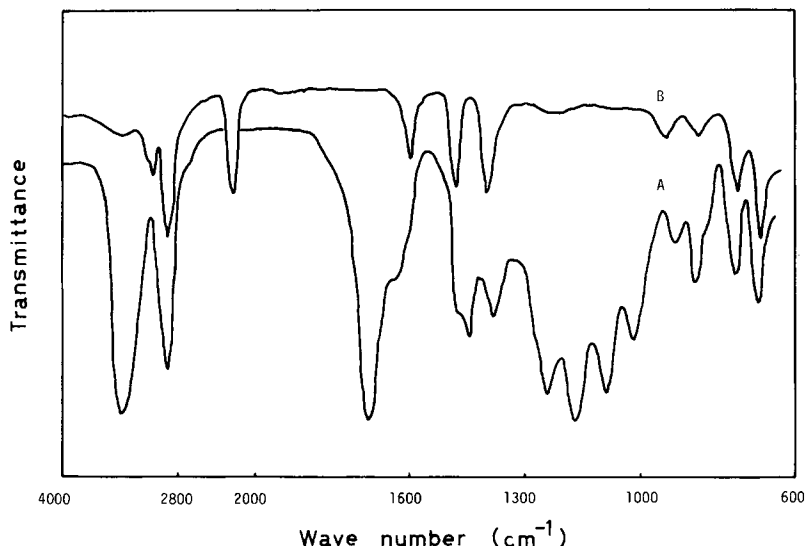
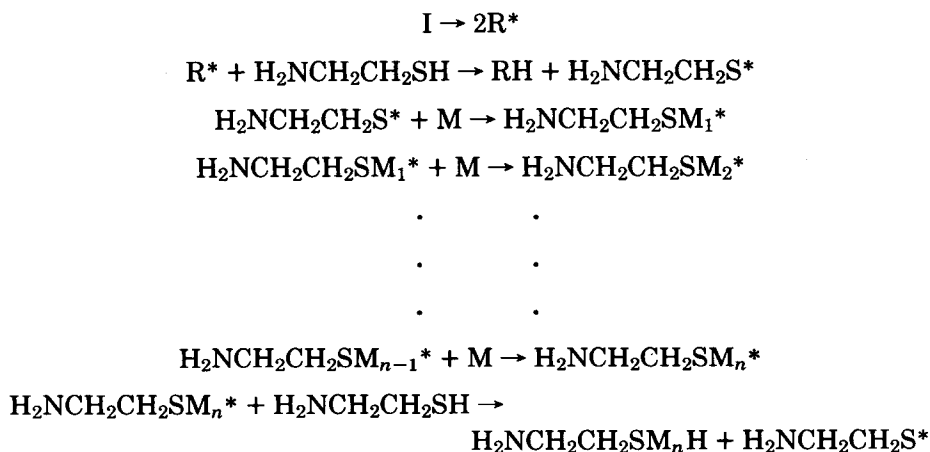


Fig. 1. IR spectra of the HEMA-St ABA-type block copolymer and the isocyanate-telechelic oligo-St: (a) HEMA-St ABA-type block copolymer; (b) isocyanate-telechelic oligo-St.

be used to synthesize the linear cooligomer, because the chain transfer constant of St was larger than that of HEMA. Cooligomers with molecular weights over a range of about 2000 to 8000 were synthesized by solution copolymerization with *n*-BuSH as chain transfer agent, as shown in Table I.

Oligomerization of HEMA with AESH as the chain transfer agent was carried out to obtain the amino-semitelechelic oligo-HEMA (prepolymer A), as shown in Table II. The molecular weights calculated from the amino group analysis as one amino group in one oligo-HEMA molecule were approximately equal to those determined from the V.P.O. measurement. This revealed that one oligo-HEMA molecule has one amino-group in one side end of the chain. It is assumed that the polymerization mechanism is the following telomerization:



Photooligomerization of St used with IPDS as an initiator was carried out to obtain the isocyanate-telechelic oligo-St (prepolymer B) as shown in Table II.

TABLE III
 ABA-type Block Copolymer

no.	Prepolymer [η] ^a	M_n	Block copolymer			
			In feed	HEMA mole fraction		[η]
Found	Calcd					
A-1	0.789	10,000	2(A-1) + B-1	0.56	0.546	1.41
A-2	0.720	3,850	2(A-1) + B-2	0.62	0.608	1.13
B-1	0.150	12,300	2(A-1) + B-3	0.75	0.744	1.19
B-2	0.123	10,500	2(A-1) + B-4	0.90	0.884	1.25
B-3	0.091	5,500	2(A-2) + B-1	0.34	0.317	1.43
B-4	0.075	2,100	2(A-2) + B-2	0.38	0.374	

^a In DMF at 30°C.

The molecular weights calculated from isocyanate group analysis as two isocyanate groups in one oligo-St were approximately equal to those determined from the V.P.O. measurement.

HEMA-St ABA-Type Block Copolymerization

Block copolymers confirmed structures could be synthesized using the method of block copolymerization, that is, telechelic oligomers were used as the prepolymer. In order to synthesize HEMA-St ABA-type block copolymers, prepolymer A was allowed to react with prepolymer B in DMF solution at 0°C for 24 hr. Prepolymer A was soluble in both methanol and isopropyl alcohol and insoluble in ether. Prepolymer B, however, was soluble in ether and insoluble in methanol and isopropyl alcohol. The purification of the ABA-type block copolymers could be performed by two steps because of different solubilities of these prepolymers. In other words, the first was precipitated from the reacted mixed solution with ether. The obtained polymer was then dried and dissolved

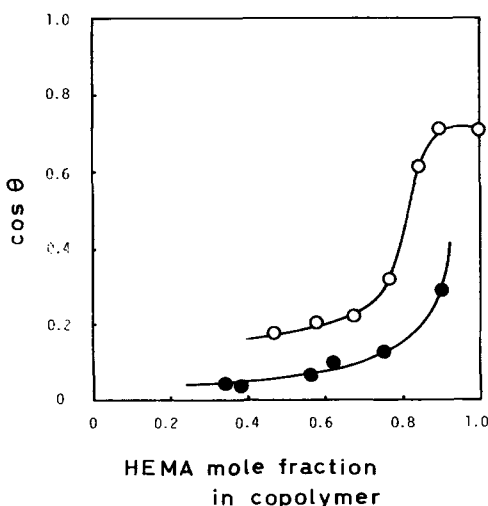


Fig. 2. Relation between wettability and copolymer composition: (●) HEMA-St ABA-type block copolymer system; (O) HEMA-St cooligomer system.

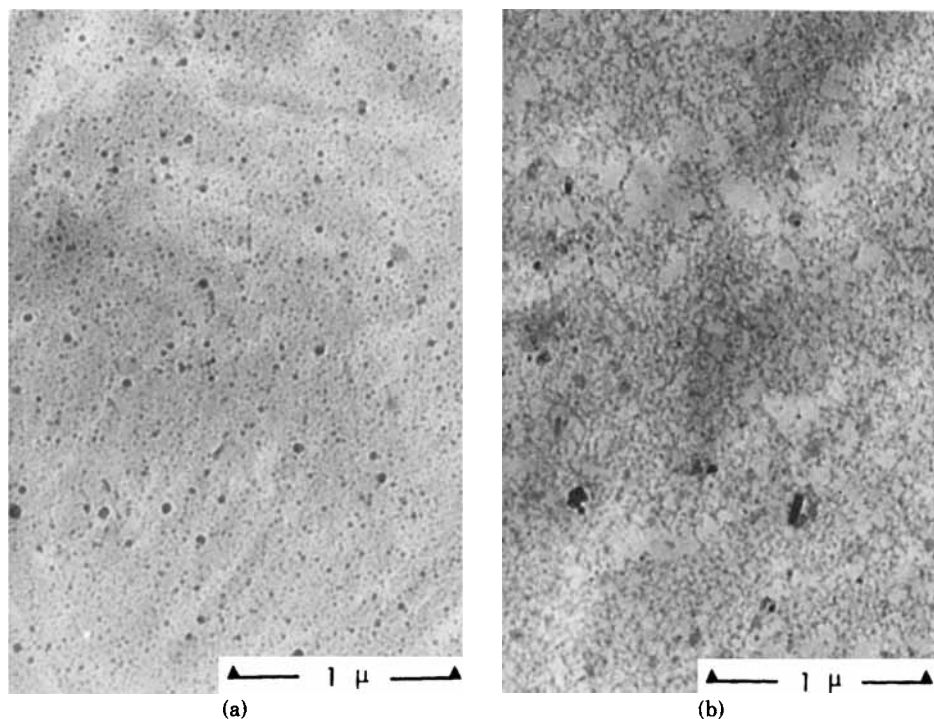


Fig. 3. Electron micrographs of HEMA-St cooligomer films cast from DMF at 40°C: (a) HEMA mole fraction 0.66; (b) HEMA mole fraction 0.81.

in DMF solvent. The second was precipitated from the DMF solution with mixed methanol-isopropyl alcohol solvent. The unreacted prepolymer B could be removed in the first step of purification, and the unreacted prepolymer A could be removed in the second step.

Figure 1 shows the IR spectra of the ABA-type block copolymer and the oligo-St. The presence of HEMA is demonstrated by the carboxyl band at 1740 cm^{-1} and many other absorptions also contained in the ABA-type block copolymer. St is also contained in the ABA-type block copolymer as indicated by the aromatic peak at 700 cm^{-1} . The isocyanate group is contained in oligo-St as indicated by the peak at 2270 cm^{-1} ; this peak, however, disappears in the ABA-type block copolymer.

Results of the ABA-type block copolymer analysis are shown in Table III. The HEMA mole fractions in the ABA-type block copolymer calculated from the ratio prepolymer A:prepolymer B = 2:1 were approximately equal to those determined from elemental analysis. The prepolymers also reacted as indicated by an increase in intrinsic viscosities of the ABA-type block copolymers compared with those of the prepolymers.

Influence of Hydrophilic and Hydrophobic Domains on Wettability

Figure 2 shows the relation between composition and wettability ($\cos \theta$) with water for the films of the random cooligomers and the ABA-type block copoly-

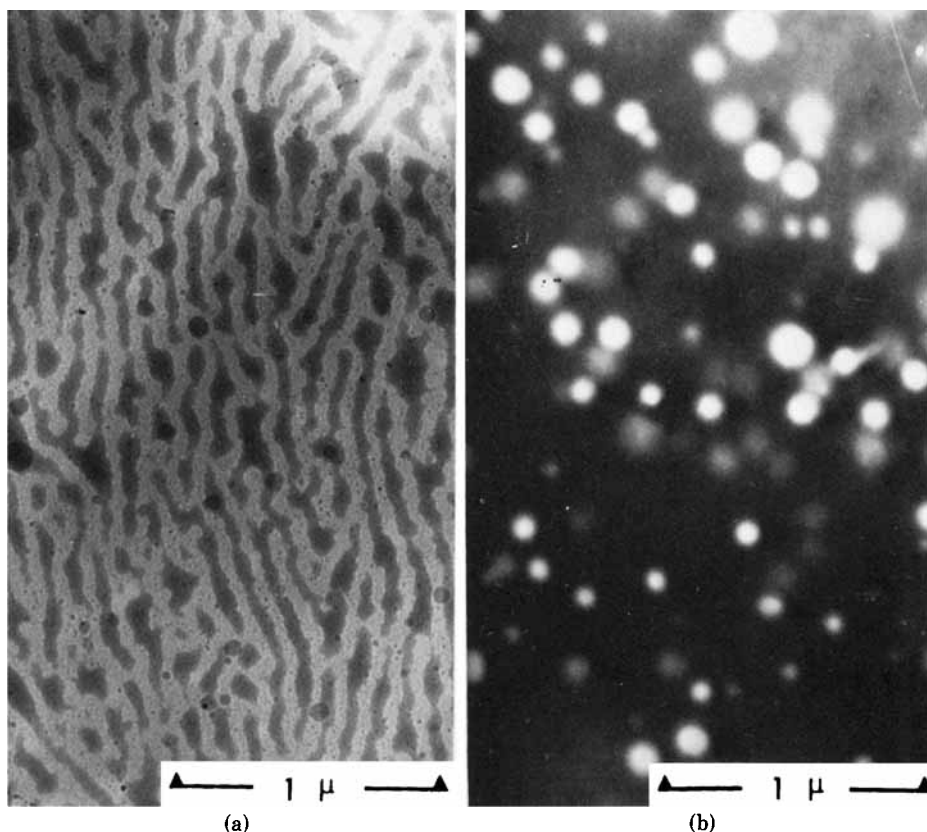


Fig. 4. Electron micrographs of HEMA-St ABA-type block copolymer films cast from DMF at 40°C: (a) HEMA mole fraction 0.61; (b) HEMA mole fraction 0.88.

mers. The wettability increased considerably with HEMA mole fraction to bring about a rise at about 0.8 HEMA mole fraction in the cooligomer system and at about 0.9 HEMA mole fraction in the ABA-type block copolymer system. The wettability of cooligomers was larger than that of ABA-type block copolymers in the same composition over the entire composition range.

The microstructures of the films of the random cooligomers and the ABA-type block copolymers could be observed by electron microscopy using osmium tetroxide fixation. The hydrophilic domains, which were composed of HEMA units, were observed as black domains and the hydrophobic domains, composed of St units, as white domains in the electron micrographs because HEMA units were fixed selectively by osmium tetroxide, as shown in Figures 3 and 4. The differences between the domain structures of the cooligomer system and the ABA-type block copolymer system are recognized by domain size and geometry.

In the random cooligomer system, hydrophilic domains were observed as spots at a HEMA mole fraction of around 0.6 (Fig. 3a), and these domain-like spots came together to form continuous geometry when HEMA mole fraction rose to around 0.8 (Fig. 3b). This result also shows that the size of hydrophilic domains of the films becomes larger with increase in HEMA mole fraction in the cooligomer composition from around 0.6 to around 0.8.

In the case of the ABA-type block copolymer system, striped hydrophilic and hydrophobic domains were observed in HEMA mole fraction around 0.6 in the copolymer composition (Fig. 4a). Hydrophobic circular domains were formed when HEMA mole fraction reached about 0.9 (Fig. 4b). This result also shows that the size of the hydrophobic domains decreases and that of the hydrophilic domains increases with increase in HEMA mole fraction in the copolymer composition from about 0.6 to about 0.9.

It is found that the domain structures, i.e., the state of aggregation of hydrophilic and hydrophobic segments, obviously is changed at a HEMA mole fraction of about 0.8 in the cooligomer system and about 0.9 in the ABA-type block copolymer system and corresponds to the remarkable rise in wettability.

The difference in wettability between cooligomers and ABA-type block copolymers was considered to be natural, since hydrophilic and hydrophobic functions were influenced not only by the composition but also by the microstructure to the polymers. These results suggest that hydrophilic and hydrophobic functions of amphiphilic polymers are largely influenced by the state of aggregation of each segment, that is, the size and geometry of hydrophilic and hydrophobic domains.

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