

Terpolymer Films Having Semipolar Structure: Preparation, Wettability, and Mechanical Properties

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ABSTRACT: A terpolymer, obtained by the free-radical terpolymerization of 2-(*N,N*-dimethylamino)ethyl methacrylate (DMMA), methyl methacrylate (MMA), and isobutyl methacrylate (IBMA), was allowed to react with hydrogen peroxide, chloroacetic acid, and diethyl sulfate to form the corresponding modified terpolymers: (1) *N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)amine *N*-oxide, MMA and IBMA (DMANO series); (2) *N*-(carboxymethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium, MMA and IBMA (CDME series); and (3) *N*-(ethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium ethylsulfonate, MMA and IBMA (EDMEES series), respectively. The terpolymer compositions were determined using ¹³C NMR spectrometry. Surface free energies of the terpolymers were

estimated by measuring the contact angles of water and methylene iodide on the three series films (DMANO, CDME, and EDMEES), and the effect of the *N*-oxide group on wettability was discussed. It was found that the upper surface of the films for the DMANO and CDME series are more hydrophobic than that for the EDMEES series. Notably, elongation to break for the DMANO series was relatively larger than that for the CDME series because of the water bound to the *N*-oxide functional group. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1235–1243, 2005

Key words: composite; mechanical property; polymer modification; polymerization; surface property

INTRODUCTION

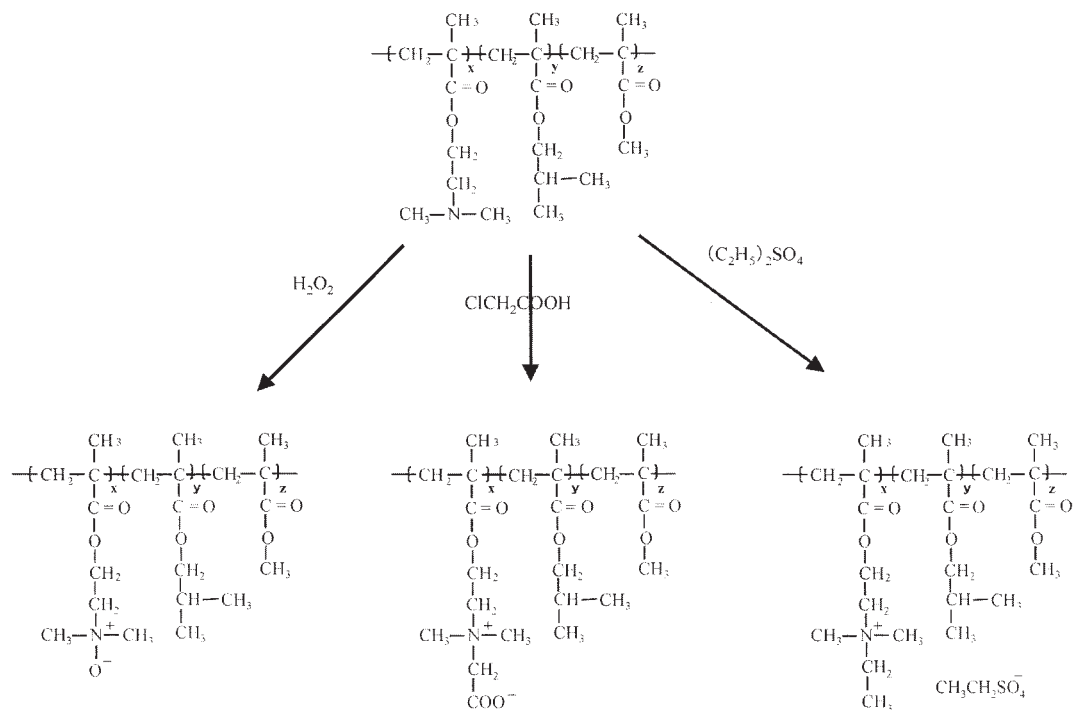
Currently, water-soluble resins can be broadly categorized as anionic, cationic, nonionic, or amphoteric resins. Methods for synthesizing water-soluble polymers have been aggressively studied at university and corporate labs. These polymers are utilized as basic materials for water treatment, reagents, pharmaceuticals, thickeners, coating agents, and cosmetics. Notably, performance in both water-solubility and humidity are demanded from the market in these polymers of cosmetics (styling spirits). So, it is necessary to know the surface properties of polymer films to investigate the two performances.

In investigating an interface-related phenomenon like film adhesion, the value of surface film tension is an important index for evaluating the performance of the film. Surface and interface tensions for liquids are measurable rather easily, while direct methods to measure surface tension (γ_s) on solid materials or interface tension (γ_{SL}) between solid and liquid have

not been established yet. As an alternative, an index to γ_s and γ_{SL} , critical surface tension to show solid wettability (γ_c), proposed by Zisman and colleagues,^{1–3} interfacial tension proposed by Fowkes⁴ or Girifalco and Good,⁵ or its modified surface tension by Owens and Wendt⁶ or Kaelble and Uy⁷, are now available. Also, recent studies are focused to the synthesis of polymers with solution viscosity behavior different from common polyelectrolytes. Examples of such polymers are amphoteric polymers,^{8–14} bearing both cationic and anionic groups separately in one molecule, and betain-type polymers,^{15–18} bearing both groups in its side chain. These polymers are called “antipolyelectrolyte,” and the electrolyte addition effect on the solution viscosity behavior of amphoteric polymers using sulfobetaine as a typical “antipolyelectrolyte” that bears both positive and negative charges in the same side chain has been vigorously studied.^{19–22} Previously, we reported the synthesis of the homopolymer of *N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)amine *N*-oxide (DMANO) and the solution properties in aqueous solutions.²³

In this study, we prepared three series terpolymers composed of: (1) *N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)amine *N*-oxide, methyl methacrylate (MMA) and

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Scheme 1

IBMA (DMANO series), as novel semipolar resins belonging to the amine oxide type; (2) *N*-(carboxymethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium, MMA and IBMA (CDME series); and (3) *N*-(ethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium ethylsulfonate, MMA and IBMA (EDMEES series); and we investigated the surface properties and mechanical properties of their antipolyelectrolyte films.

EXPERIMENTAL

Materials

Commercial 2-(*N,N*-dimethylamino)ethyl methacrylate (DMMA), isobutyl methacrylate (IBMA), and methyl methacrylate (MMA) as a monomer (Mitsubishi Rayon) and ethanol (Japan Ethanol) were purified by distillation. Dimethyl 2,2-azobis(2-methylpropionate) as an initiator (Wako Pure Chemical), hydrogen peroxide (Mitsubishi Gas Chemical), diethyl sulfate (Wako Pure Chemical), and chloroacetic acid (Mitsui Chemicals) were used without further purification. Anionic exchange resin based on sodium sulfonate polystyrene (Mitsubishi Chemicals PA416) and cationic exchange resin based on quarternary ammonium chloride polystyrene (Mitsubishi Chemicals PK220) were used to remove inorganic salts

Preparation of terpolymers

50 wt % ethanol solutions of three different DMMA/IBMA/MMA ratios in monomer feeds in a 2L fully

dried three necked flask, equipped with a thermometer, nitrogen inlet, and mechanical stirrer, were prepared, and 0.5 wt % (against total monomers) dimethyl 2,2-azobis(2-methyl)propionate was added as an initiator. Nitrogen was introduced into the solution at 35°C for 30 min at the flow rate of 100 mL/min, followed by step-by-step increase of temperature up to 80°C during 1 hr. The solution was kept at the same temperature for 9 h to complete polymerization. After completion of the reaction, the reaction mixture was added to a large amount of methanol to precipitate the polymer. The resulting polymer was filtered and dried under reduced pressure until a constant weight. The weight-average molecular weight (M_w) of the polymers was determined to be 91,000–97,000.

Modification of polymers

N,N-Dimethyl-*N*-(2-methacryloyloxyethyl)amine *N*-oxide/IBMA/MMA terpolymer (*N*-oxide-type, DMANO series: DMANO-30, 40, 50). 40 wt % ethanol solutions of terpolymers prepared in three different monomer feed ratios were placed in a fully dried three necked flask, equipped with a thermometer, nitrogen inlet, and mechanical stirrer, and were warmed up to 80°C. Equivalent molar hydrogen peroxide per DMMA in 30 wt % aqueous solution was added drop-by-drop onto the solution during 1 h, and then stirred for 24 h. After completion of the reaction, an excess amount of acetone was added to the reaction mixture to obtain a solid product. The products (95–98% yield) were dried under reduced pressure until a constant weight was attained.

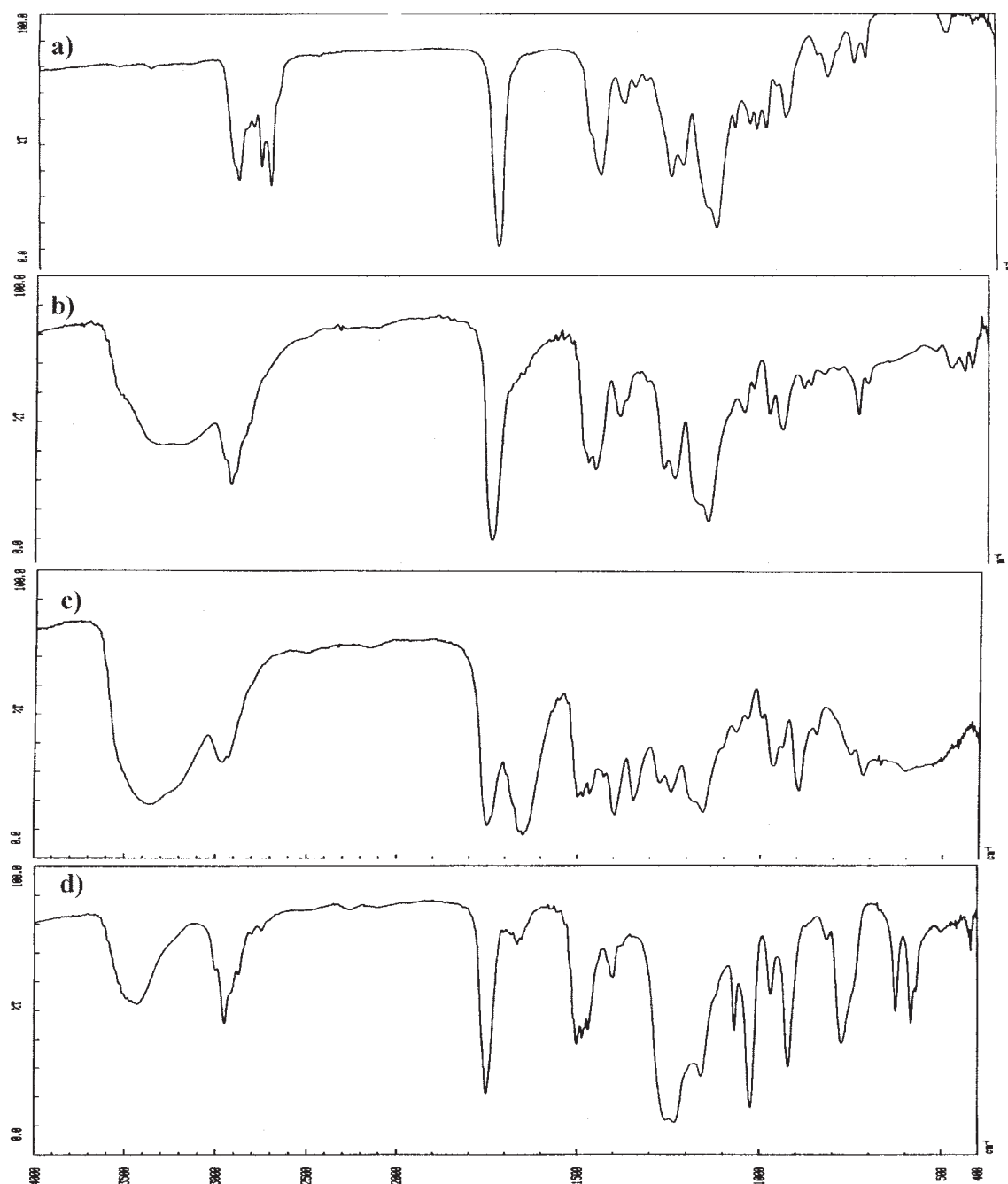


Figure 1 FT-IR spectra of terpolymers (films) in: a) DMMA-30, b) DMANO-30, c) EDMEEES-30, and d) CDME-30.

N-Carboxymethyl-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium/IBMA/MMA terpolymer (carboxybetain-type, CDME series: CDME-30, 40, 50). 40 wt % ethanol solutions of terpolymers prepared in three different monomer feed ratios were placed in a fully dried three necked flask, equipped with a thermometer, nitrogen inlet, and mechanical stirrer, and warmed up to 80°C. 1.2 equivalent molar of potassium chloroacetate per 1.0M DMMA unit in 20 wt % ethanol suspension was added drop-by-drop onto the solution during 1 h, and then stirred for 30 h. After filtrating out precipitated potassium chloride,

the filtrate was passed through an anion exchange resin (PA416) and then a cationic exchange resin (PK220) to reduce the amount of inorganic salt less than 10 ppm. The filtrate was then added into an excess amount of acetone to obtain a solid product. The products (90–95% yield) were dried under reduced pressure until a constant weight was attained.

N-Ethyl-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium ethylsulfonate/IBMA/MMA terpolymer (ethyl cation-type, EDMEEES series: EDMEEES-30, 40, 50). 40 wt % ethanol solution of terpolymers prepared in three dif-

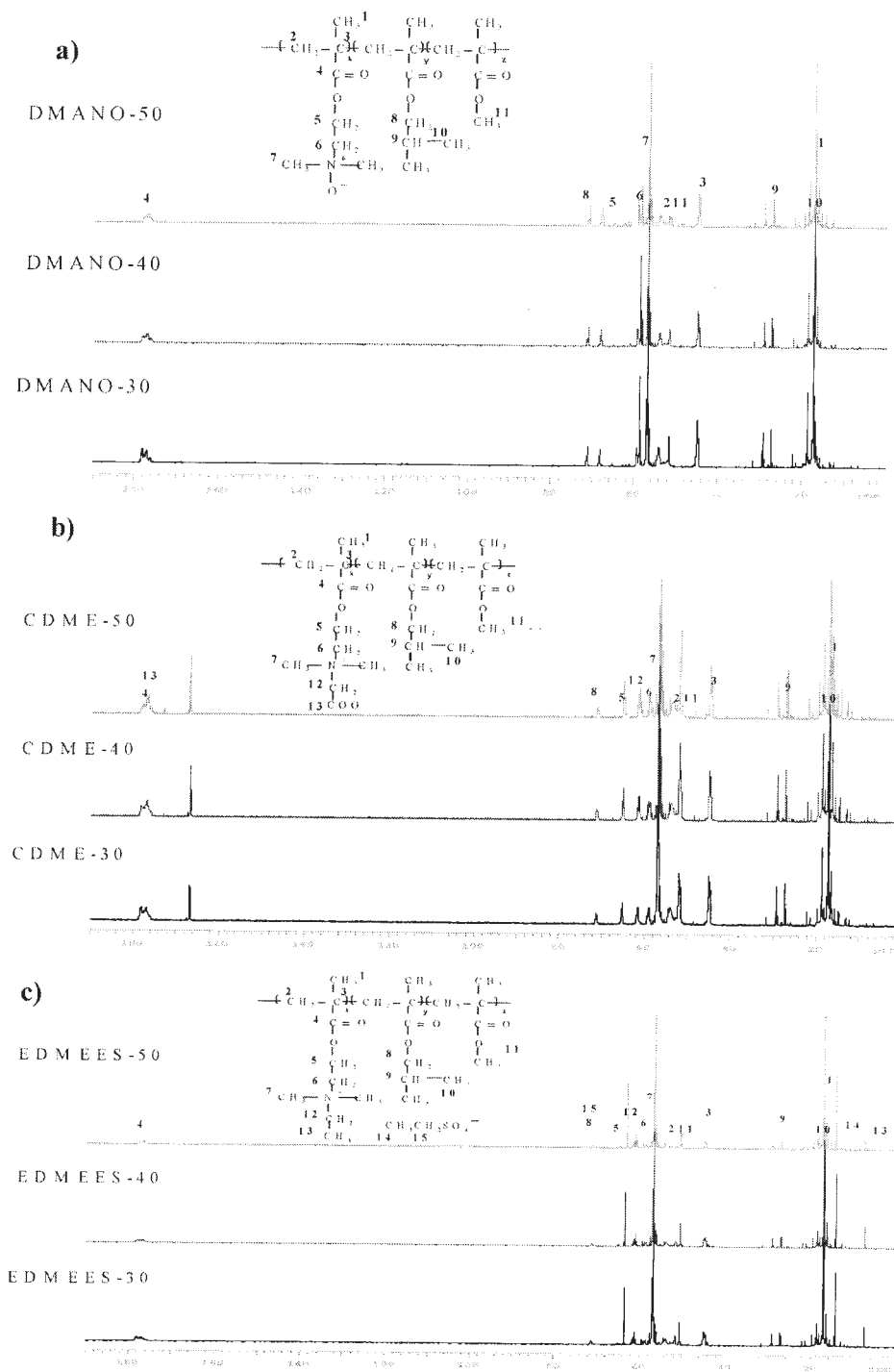


Figure 2 ^{13}C NMR spectra in ethanol/ D_2O (80/20 v/v) of the: (a) DMANO series, (b) EDMEES series, and (c) CDME series.

ferent monomer feed ratios were placed in a fully dried three necked flask, equipped with a thermometer, nitrogen inlet, and mechanical stirrer, and warmed up to 80°C . 1.0 equivalent molar of diethyl sulfate per 1.0M equivalent of DMMA unit was added drop-by-drop onto the solution during 1 h and then stirred for 10 h. After completion of the reaction, the reaction mixture was added into an excess amount of acetone

to obtain a solid product. The products (95–97% yield) were dried under reduced pressure until a constant weight was attained.

Measurements

^{13}C NMR spectra of the terpolymers were taken on a Varian UNITY plus 400 MHz FT NMR spectrometer in

TABLE I
Terpolymer Composition of the DMANO, CDME, and EDMEEES series

Sample	Monomer feed ratio (mol %)			Polym. Compn. (mol %)		
	DMMA	IBMA	MMA	DMMA	IBMA	MMA
DMANO-30	31	19	50	31	20	49
DMANO-40	42	20	38	40	20	39
DMANO-50	53	22	25	50	22	28
CDME-30	31	19	50	36	18	45
CDME-40	42	20	38	44	19	37
CDME-50	53	22	25	59	21	19
EDMEES-30	31	19	50	38	20	42
EDMEES-40	42	20	38	47	20	34
EDMEES-50	53	22	25	57	21	22

ethanol/D₂O (80/20 v/v) with a concentration of 20 wt/vol % at 50°C with ethanol (CH₂ = 56.8ppm) as an internal standard. Measurement was carried out with an accumulation of 4096 times in total at the pulse intervals of 15 s. FT-IR spectra were obtained on a JASCO International IR-700 spectrometer at 25°C with a casting film on a KBr plate. TG-DTA data were obtained on a Seiko Instruments TG-DTA 200 apparatus operated under a flowing nitrogen (50 mL/min) atmosphere. The 20 mg amount of the terpolymer sample was typically weighted into an aluminum pan and measured in a range of 30–300°C at a heating rate of 0.7°C/min. Number-average (M_n) and weight-average (M_w) molecular weights of the terpolymers were estimated by gel permeation chromatography (GPC) on a TOSOH Instruments 8020 equipped with TOSOH refractive index detector and three TOSOH TSK-gel columns (G6000HXL, G4000HXL, and G2500HXL) using tetrahydrofuran (THF) as an eluent and polystyrene standards for calibration at room temperature.

The contact angle on the films was measured as follows: 20% ethanol solution of each terpolymer in the three terpolymer series (DMANO-30, 40, 50, CDME-30, 40, 50, and EDMEEES-30, 40, 50) were cast on Teflon sheet using 100 μ m-depth applicator to ob-

tain a film, which was dried 2 h at 50°C and then kept under 60% humidity conditions at 23°C for 24 h. A drop of water or methylene iodide was placed on the film, and after 5 s the contact angle was measured. On the measurement, the video imaging pictures taken by CCD camera were used to obtain a more accurate contact angle. The contact angle for each specimen was measured five times, and the average value was cited.

Mechanical properties of terpolymers

A 30% ethanol solution of polymer was cast on the Teflon sheet using a 200 μ m-depth applicator and air-dried. The resulting film was cut into 15 mm width, dried at 50°C for 2 h, and kept at 23°C under 60% humidity conditions for 24 h, and then the film was cut into 8 cm in length to use as a specimen. The specimen thickness was measured at three separate points around the central part of the film, and the smallest value among the three was adopted as the specimen thickness. A stress-strain curve was measured using a Rheometer FUDOH NRM-2003J. The upper and lower edges of the film were fixed to two adaptors mutually 50 mm off (the effective specimen

TABLE II
Contact Angles, Surface Free Energies, and Mechanical Properties of the Terpolymers

Sample	Contact angle		Surface free energy (γ_s)	Mechanical properties			
	θ_1	θ_2		Elongation at yield (%)	Elongation to break (%)	Tensile strength (MPa)	Young's modulus (MPa)
DMANO-30	80	46	37.5	9	31	23	474
DMANO-40	84	46	37.0	10	41	18	342
DMANO-50	85	46	36.8	12	88	11	196
CDME-30	76	45	38.8	6	6	28	627
CDME-40	77	46	38.2	6	6	26	598
CDME-50	69	45	41.4	7	7	24	434
EDMEES-30	79	45	38.1	9	54	14	323
EDMEES-40	40	47	57.8	14	248	5	128
EDMEES-50	30	45	63.7	48	343	1	30

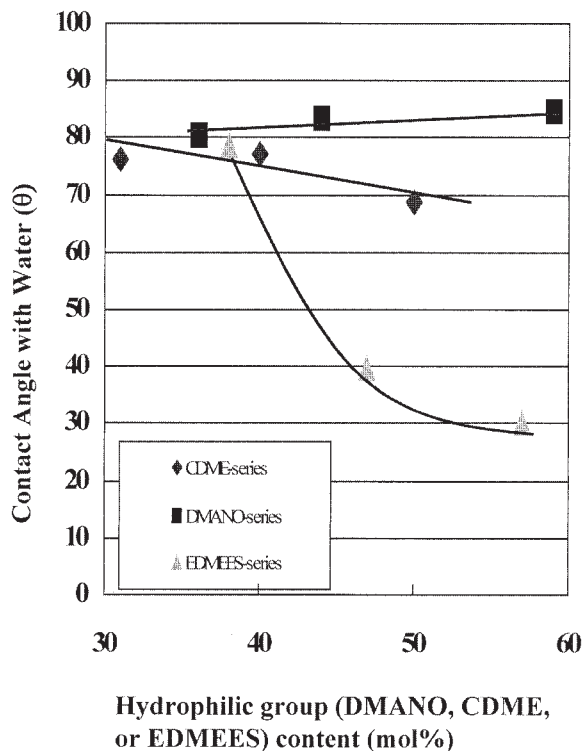


Figure 3 The relationship of the hydrophilic group contents with the contact angles of water for the DMANO series, CDME series, and EDMEES series.

length), and the specimen to be examined on the rest moved at the velocity rate of 2 cm/min (velocity for tensile strength study). The experiment for each specimen was carried out five times, and each experiment ended at the time when the specimen came to be broken. The value of the expanded length was plotted against the tensile strength to obtain the stress-strain curve. The values of the elongation at yield, elongation to break, tensile strength, and Young's modulus were calculated according to the equation as shown in the literature.²⁴

RESULTS AND DISCUSSION

Modification of polymer and characterization

Three kinds of terpolymers were obtained by terpolymerization at the DMMA/IBMA/MMA ratios in monomer feed of 31/19/50, 42/20/38, and 53/22/25 in mol %, respectively, in ethanol at 80°C for 10 h under nitrogen using a radical initiator. The polymers were obtained as white powders, with molecular weight distribution of 3.0–3.6 and weight-average molecular weight of 91,000–97,000. Resulting terpolymers were reacted with hydrogen peroxide, potassium chloroacetate, and diethyl sulfate to form corresponding modified terpolymers

(*N*-oxide-, carboxybetain-, and ethyl cation-type), respectively (Scheme 1).

Figure 1 shows the IR spectra of the base polymer with the DMMA/IBMA/MMA ratio of 31/19/50 in mol % and of the modified terpolymers, DMANO-30, CDME-30, and EDMEES-30.

In Figure 1a, absorption bands at 2950, 2800, 1730, 1450, 1240, and 1150 cm^{-1} were assigned to the stretching vibrations of $\nu_{\text{C-H}}$, $\nu_{\text{N-CH}_3}$, $\nu_{\text{C=O}}$, $\nu_{\text{C-H}}$, $\nu_{\text{C-O-C}}$, and $\nu_{\text{C-O-C}}$, respectively. In Figure 1b, on *N*-oxidation, the absorption band at 2800 cm^{-1} due to the *N-CH*₃ disappeared, and instead two new signals, assigned to for *N-O*, appeared at 3350 and 960 cm^{-1} . In Figure 1c, the absorption band at 2800 cm^{-1} due to the *N-CH*₃ disappeared, and instead a new band assigned to C=O of ester appeared at 1650 cm^{-1} , which evidenced the proceeding of the carboxybetain reaction. Also, in Figure 1d, the disappearance of the absorption band at 2800 cm^{-1} due to *N-CH*₃ evidenced the proceeding of the ethyl cation reaction.

The analysis of the terpolymer using the ¹H NMR method was difficult because of the overlapping of some of the peaks. Thus, we used analysis by the ¹³C NMR method instead of the ¹H NMR one, and a mixed solvent of ethanol/D₂O (80/20 v/v) was used for the measurement. ¹³C NMR spectra of *N*-oxide-type, carboxybetain-type, and ethyl cation-type ter-

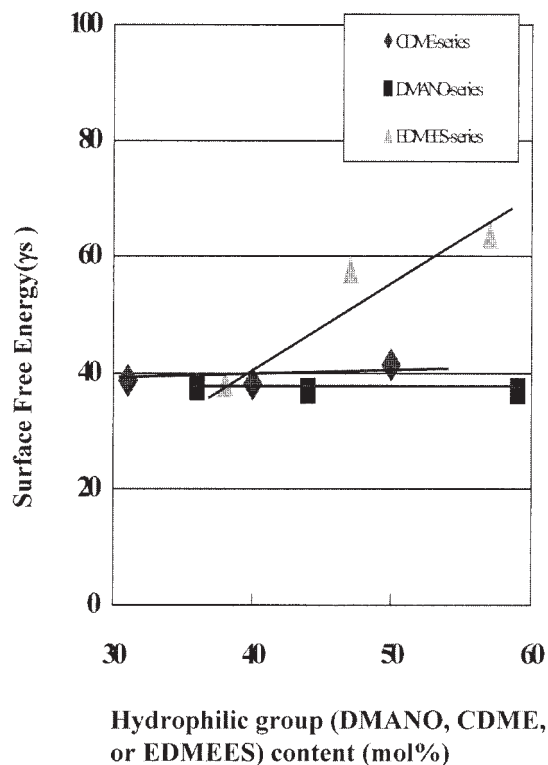
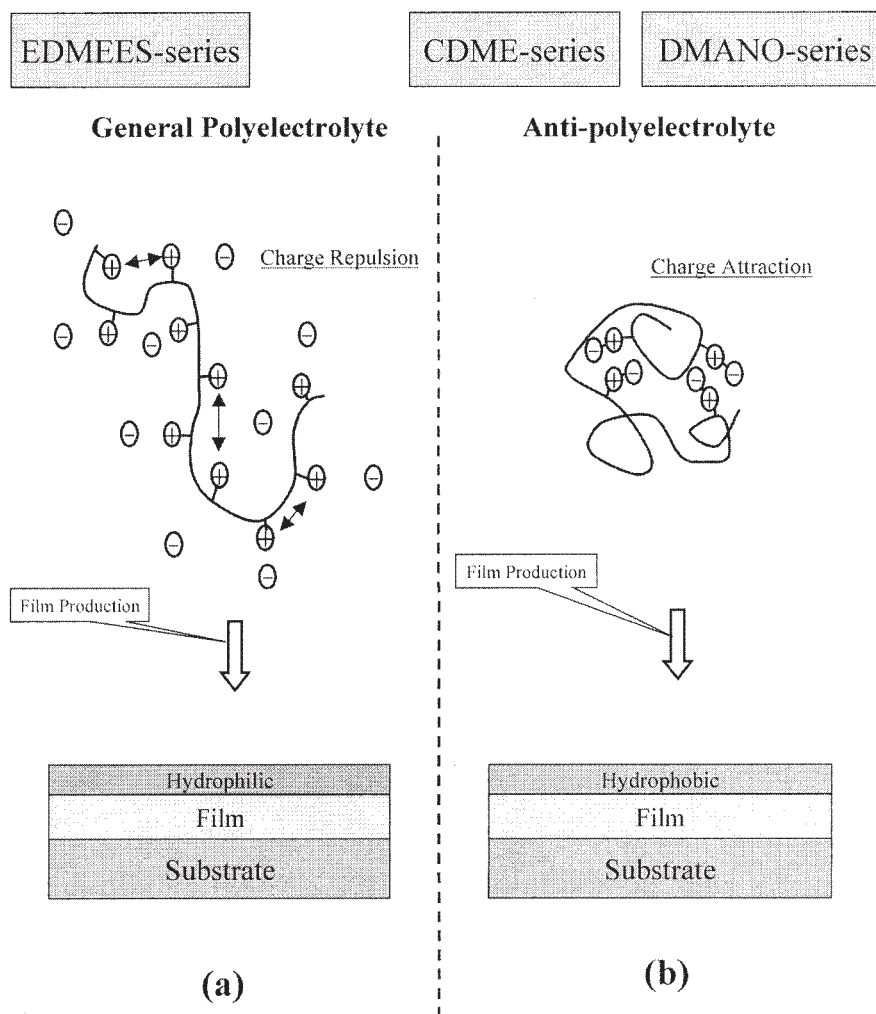


Figure 4 The relationship of the hydrophilic group contents with the surface free energy of water for the DMANO series, CDME series, and EDMEES series.



Scheme 2

polymers are shown in Figures 2a, 2b, and 2c, respectively.

Each peak was assigned to the respective carbons of the chemical structure illustrated therein. Signals of 68, 65, and 61 ppm in the spectra were assigned to the carbon of the OCH₂ group of the DMANO and CDME series, and the NCH₂ group of the EDMESS series, respectively; and a signal of 27 ppm of the DMANO series was assigned to the carbon of the CH group from IBMA, and signals of 71 ppm of the CDME and EDMESS series were assigned to the carbon of the OCH₂ group from IBMA, respectively. Isolated signals from MMA were not observed even under the above condition, and the amount of MMA was calculated by subtracting integrated monomer values from the C=O value (around 177 ppm) for methacrylate. The composition of the three different terpolymers (either *N*-oxide-, carboxybetain- or ethyl cation-type) obtained by modification of the terpolymers prepared from DMMA, IBMA, and MMA was determined according to the method shown in the literature.⁸ Table

I shows the compositional ratios of the three terpolymer series, which were obtained from the method mentioned above. Terpolymer composition was almost the same as that in monomer feed.

Surface free energy of polymer film

To investigate surface properties of terpolymer films prepared, the surface tension of a liquid on a polymer film was evaluated. The surface tensions of water and of methylene iodide can be obtained as a sum of a dispersion force (γ_W^d and γ_L^d) and a polar one (γ_W^p and γ_L^p), as shown in eqs. (1) and (2):

$$\gamma_W = \gamma_W^d + \gamma_W^p \quad (1)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (2)$$

Here, γ_W^d and γ_W^p of water are reported to be 21.8 and 51.0 mN/m, and γ_L^d and γ_L^p to be 48.5 and 2.3 mN/m, respectively.⁷

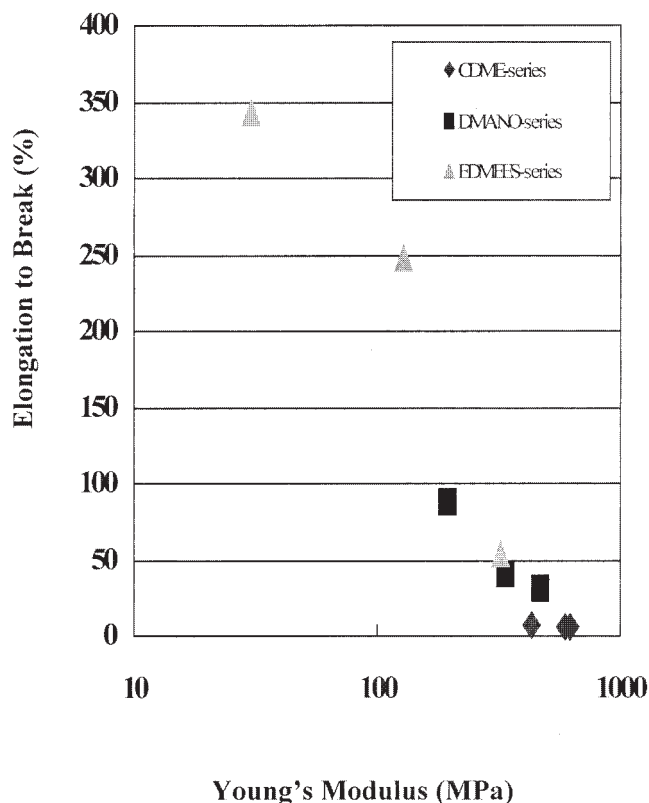


Figure 5 Relationship between Young's modulus and elongation at break for the DMANO series, CDME series, and EDMES series.

$$\gamma_w(1 + \cos\theta_1) = 2\sqrt{\gamma_s^d\gamma_w^d} + 2\sqrt{\gamma_s^p\gamma_w^p} \quad (3)$$

$$\gamma_L(1 + \cos\theta_2) = 2\sqrt{\gamma_s^d\gamma_L^d} + 2\sqrt{\gamma_s^p\gamma_L^p} \quad (4)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (5)$$

By measuring the contact angles of water (θ_1) and methylene iodide (θ_2) on the polymers and solving eqs. (3) and (4) for two unknowns, γ_s^d and γ_s^p , it is easy to find the total surface tension of the polymer from eq. (5). Table II summarizes the contact angles of water and methylene iodide on the polymer films of DMANO-30, 40, 50, CDME-30, 40, 50, and EDMES-30, 40, 50 in air and their obtained total surface tensions (surface free energies).

Figure 3 shows the relationship of the contact angle of water with the content (mol %) of hydrophilic groups such as *N*-oxide, carboxybetain, and ethyl cation in the DMANO, CDME, and EDMES series. The contact angles of the terpolymers tends to decrease with increasing the content of the hydrophilic group, in particular, the contact angles of the EDMES series decreased more markedly than those of the DMANO and CDME series to reach smaller angle values. Figure 4 shows the relationship of the surface free energy (γ_s) with the content of the hydrophilic group. It was

found that the surface energies ($\gamma_s = 36\text{--}41$) of the DMANO and CDME series showed an almost constant value despite the increased hydrophilic group content, while the surface free energy of the EDMES series increased with increasing the content of the hydrophilic group. This suggests that the upper surface of the DMANO and CDME series films is hydrophobic, while that of the EDMES series ones is hydrophilic. This behavior is explained as follows: As shown in Scheme 2, the films prepared from common polyelectrolytes, such as the EDMES series, become much more hydrophilic because they tend to expand by the charge-charge repulsion, whereas the films prepared from antipolyelectrolytes, such as the DMANO and CDME series, having both positive and negative charges in one molecule, become hydrophobic because they tend to shrink by mutual charge attraction in a water solution (Scheme 2).

Mechanical properties

The mechanical properties of terpolymers were studied based on the measurement of their tensile strength (stress-strain curves). Table II shows the data of elongation at yield, elongation to break, tensile strength, and Young's modulus. Figures 5 and 6 show the relationships of Young's modulus with elongation to

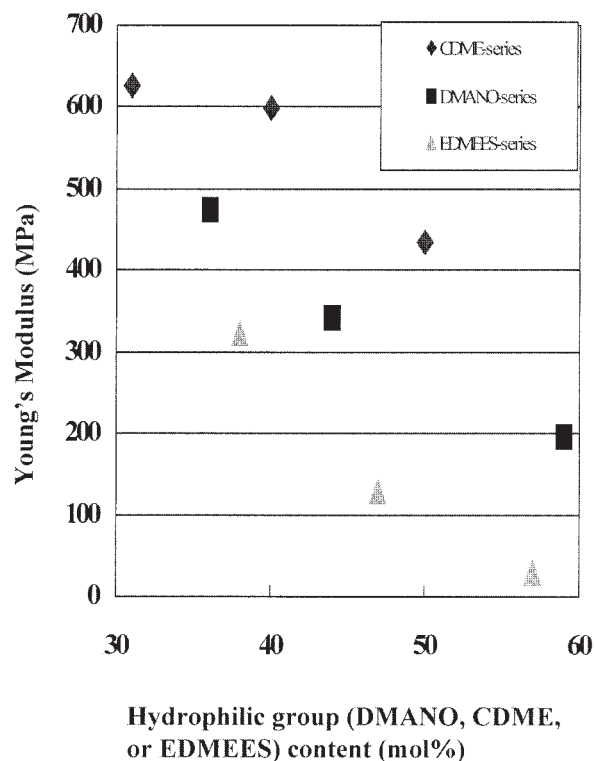


Figure 6 Effect of hydrophilic group content on the Young's modulus for the DMANO series, CDME series, and EDMES series.

break, and of Young's modulus with the hydrophilic group content in the DMANO, CDME, and EDMEES series, respectively. Young's modulus of the terpolymer series decreases from 474 to 196 MPa for the DMANO series, from 627 to 434 MPa for the CDME series, and from 323 to 30 MPa for the EDMEES series with increasing the hydrophilic group content from 31 to 59 mol %, respectively. On the other hand, the value of elongation to break increases from 31 to 88% for the DMANO series and from 54 to 343% for the EDMEES series, respectively, but do not change for the CDME series. In particular, the marked increase of elongation to break for the EDMEES series is notable, due to fact that the hygroscopic property of the film depends upon the ion intensity of the cationic functional groups. When the mechanical properties of the DMANO series are compared with those of the CDME series, the former has a larger elongation to break and smaller Young's modulus than the latter, respectively, even though both glass transition temperatures (T_g) are similar (DMANO-40 (55°C) and CDME-40 (60°C)). From TG-DTA measurement for these three terpolymers (DMANO-, CDME-, EDMEES-40), 10% weight loss was observed at around 100°C for the DMANO series film, but not for the CDME and EDMEES series films. This indicates that the DMANO series contains hydrated water, but both the CDME and EDMEES series do not contain hydrated water. It was reported that a surfactant having a semipolar functional group such as dimethyldodecylamine *N*-oxide contains the hydrated water.²⁵⁻²⁶ It is considered that as the DMANO series has the semipolar group, the polymer retains the same property as the above-mentioned surfactant. It is concluded, therefore, that DMANO series films show larger elongation to break and smaller Young's modulus than CDME series films because of the existence of hydrated water as a plasticizer.

CONCLUSIONS

A terpolymer, obtained by the terpolymerization of 2-(*N,N*-dimethylamino)ethyl methacrylate (DMMA), methyl methacrylate (MMA), and isobutyl methacrylate (IBMA), was allowed to react with hydrogen peroxide, chloroacetic acid, and diethyl sulfate to form the corresponding modified terpolymers: (1) *N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)amine *N*-oxide, MMA and IBMA (DMANO series); (2) *N*-(carboxymethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium, MMA and IBMA (CDME series); and (3) *N*-(ethyl)-*N,N*-dimethyl-*N*-(2-methacryloyloxyethyl)ethyl ammonium ethylsul-

fonate, MMA and IBMA (EDMEES series), respectively. Using ¹³C NMR analysis, terpolymer composition was confirmed to have the same composition as the monomers (starting materials) reacted. Based on the observation of the surface free energies of the terpolymers, which were obtained from the data of water contact angle and methylene iodide on the films, it was found that the upper surface of the films for the DMANO and CDME series are more hydrophobic than that for the EDMEES series. The comparison of mechanical properties by the stress-strain test between two specimens clarified that the DMANO series was a unique polymer having larger elongation to break (smaller Young's modulus) than the CDME series due to the existence of hydrated water in the DMANO series.

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