

# Synthesis and Characterization of Novel Sulfobetaines Derived from 2,4-Tolylene Diisocyanate

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**ABSTRACT:** Novel sulfobetaines were synthesized from two urethanes derived from 2,4-tolylene diisocyanate (TDI) blocked with 2-hydroxyethyl methacrylate (HEMA) and either *N,N*-dimethylaminopropylamine (DMAPA) or *N,N*-dimethylaminoethanolamine (DMAEA). The first-stage reaction of TDI with HEMA was carried out in petroleum ether heterogeneously with the precipitation of the intermediate monoadduct product in the reaction solution. The second stage is a homogeneous reaction of the monoadduct with the blocking agent, DMAPA or DMAEA, in tetrahydrofuran (THF). In both reactions, an inhibitor, hydroquinone, and a catalyst, dibutyltin diacetate (DBDac), were used. The tertiary amine urethanes were quaternized by 1,3-propane sultone to form the two novel sulfobetaines. The results of the elemental analysis of those products along with their <sup>1</sup>H-NMR and IR spectra indicated that these materials were, indeed, the compounds expected. The products dissolved in strongly polar organic solvents. The copolymerization of these two monomers with comonomers such as styrene, methyl methacrylate, acrylamide, and HEMA was investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3447–3459, 2001

**Key words:** 2,4-tolylene diisocyanate; 2-hydroxyethyl methacrylate; sulfobetaine

## INTRODUCTION

Introducing ions into polymeric materials is a useful way to alter the polymer morphology and physical properties. Synthesis and limited mechanical data were reported for polyurethane (PU) ionomers by Dieterich et al. in 1970.<sup>1</sup> PU ionomers can be prepared by reaction of a chain extender containing an amino group with a NCO-terminated PU prepolymer and subsequent modification with an ionizable component. There are three types of PU ionomers: (1) a cationomer formed from a tertiary amine followed by reaction with an alkyl halide; (2) an anionomer formed

from a secondary amine followed by a reaction with a sultone or lactone; and (3) a zwitterionomer formed from a tertiary amine followed by reaction with a sultone to form a quaternary ammonium sulfonate.

PUs have received a fair amount of attention as polyelectrolytes.<sup>2–6</sup> Extensive work has been done in the development of water-based anionic PUs<sup>2–6</sup> and cationomeric PUs.<sup>7,8</sup> Syntheses of cationomeric PUs<sup>9–13</sup> were carried out in different ways and with a wide variety of reactants. The effect of the addition of deionized water to the cationomers on their viscosity was reported.<sup>7,8,10</sup> Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies on aqueous cationomeric PU systems were reported in specific cases.<sup>10</sup>

Data regarding PUs with a sulfobetaine structure in the polymer backbone, most of all showing the influence of zwitterionization on the morphol-

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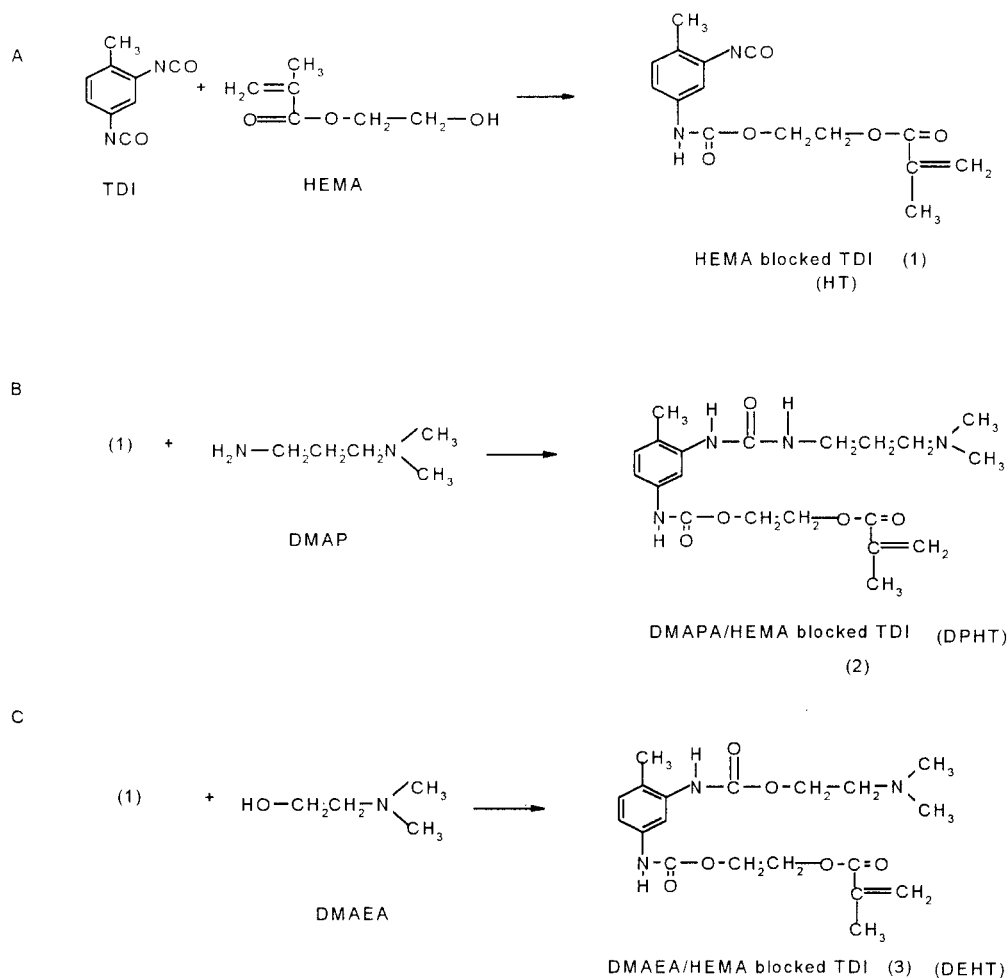
**Table I** Chemicals Used in Preparing the Blocked Diisocyanate Monomers

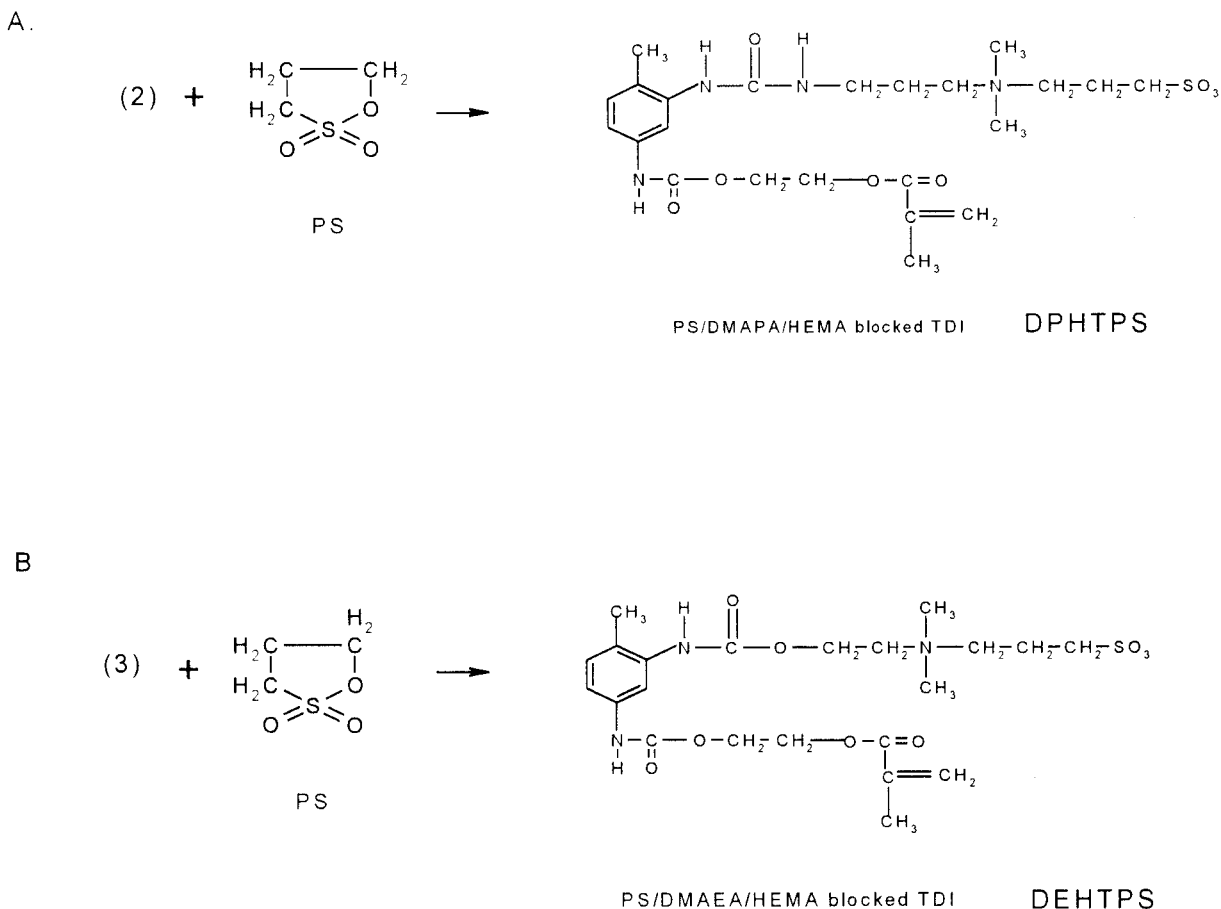
Procedure	First Stage <sup>a</sup>			Second Stage <sup>b</sup>			
	Blocking Agent 1 (g)	Inhibitor (g)	DBDAc (g)	Blocking Agent 2 (g)	Inhibitor (g)	DBDAc (g)	THF (mL)
1	HEMA 13.0	0.065	0.02	DMAPA 12.2	0.065	—	100
2	HEMA 13.0	0.065	0.02	DMAEA 10.7	0.065	0.02	100
3	DMAPA 10.2	—	—	—	—	—	—
4	DMAEA 8.9	—	0.02	—	—	—	—

<sup>a</sup> The TDI amount: 17.4 g.<sup>b</sup> The petroleum ether amount: 100 mL.

ogy and physical properties of the polymers comparatively with nonionic PUs, were presented by Cooper and coworkers.<sup>14–16</sup> Taking into account

the possible electrostatic interactions between metal ions and sulfobetaine functionalities, significant modifications in the polymer solution,

**Scheme 1** Scheme mode for the two-stage method of the blocked TDI.



**Scheme 2** Reaction of novel sulfobetaine derived from tertiary amine urethane.

film properties, and photochemical behavior can be induced by incorporation of metal salts in the polymers.<sup>17–20</sup>

The monomeric diisocyanates are too toxic to be used as such, so they are generally formulated into prepolymer systems by reaction with diols, polyols, or diamines. 2-Hydroxyethyl methacrylate (HEMA)-blocked 2,4-toluene diisocyanate (TDI) was reported on elsewhere.<sup>21,22</sup>

Hence, the two isocyanate groups of the TDI molecule were blocked by two different blocking agents, HEMA and either *N,N*-dimethylamino-propylamine (DMAPA) or *N,N*-dimethylamino-ethanolamine (DMAEA), to prepare two tertiary amine urethane monomers. The tertiary amine urethanes were then quaternized with 1,3-propane sultone (PS) to form the two novel sulfobetaines. The <sup>1</sup>H-NMR spectra, the solubility, and the polymerization behavior of both novel sulfobetaines were investigated in this study.

## EXPERIMENTAL

### Materials

TDI (Fluka, Switzerland), DMAPA (TCI, Tokyo, Japan), DMAEA (TCI), 1,3-propane sultone (PS; TCI), hydroquinone (Kodak), and dibutyltin diacetate (DBDAC; TCI) were used as received. HEMA (TCI) was further purified by vacuum-distillation at 68°C/5 mmHg. Acetone (ALPS, Taiwan), butanone (TCI), tetrahydrofuran (THF; ALPS), dimethyl sulfoxide (DMSO; TCI), dimethylformamide (DMF; TCI), dimethylacetamide (DMAc; TCI), ethyl ether (Fluka), and petroleum ether (Fluka) used as solvents were dried and stored over 3 Å molecular sieves.

### Synthesis of Monoadducts (First Stage)

The amounts of chemicals used in each of these preparations are listed in Table I. The steps for the two-stage reaction are illustrated in Scheme

**Table II Yield and Melting Point of the Blocked Monomers**

Sample	Yield (g)	Mp (°C)	Theory Yield (g)	Yield (%)
HEMA-blocked TDI	28.9	62.0	30.4	95.0
DMAEA-blocked TDI	24.9	65.0	26.3	94.5
DMAPA/HEMA-blocked TDI	32.6	92.0	40.6	80.2
DMAEA/HEMA-blocked TDI	27.7	96.0	39.3	70.6
PS/DMAPA/HEMA-blocked TDI	10.7	—	15.8	68.0
PS/DMAEA/HEMA-blocked TDI	14.1	—	15.5	91.0

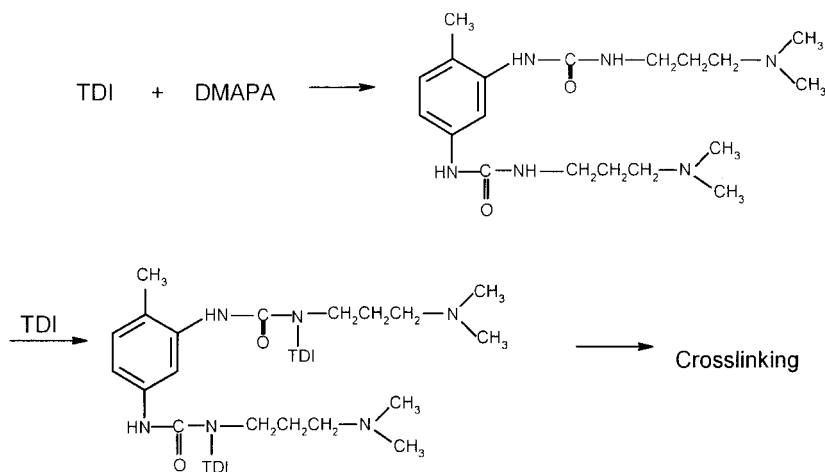
1. In the first stage, the flask was initially charged with petroleum ether and the inhibitor, hydroquinone, was added with constant stirring. TDI was allowed to mix with the solvent and the inhibitor for about 10 min before HEMA was added. HEMA was added dropwise through an addition funnel. At the start of the HEMA addition, the catalyst DBDac was also added. It took about 1 h to complete the HEMA addition. The reaction of HEMA with TDI was slightly exothermic. As a result, the temperature increased to 30°C. During the addition of HEMA, the intermediate monoadduct product precipitated from the solution. After the HEMA addition was completed, the reaction was allowed to continue for another 2 h.

The solid white monoadduct was washed three times in the flask with petroleum ether to remove unreacted TDI and HEMA. The monoadduct was dried at 30°C in a vacuum oven for 1 day. The monoadduct was analyzed by elemental analysis, NMR, and IR spectroscopy. The yield and melting point of the monoadduct product were 96% and 62°C, respectively [see Scheme 1(A)].

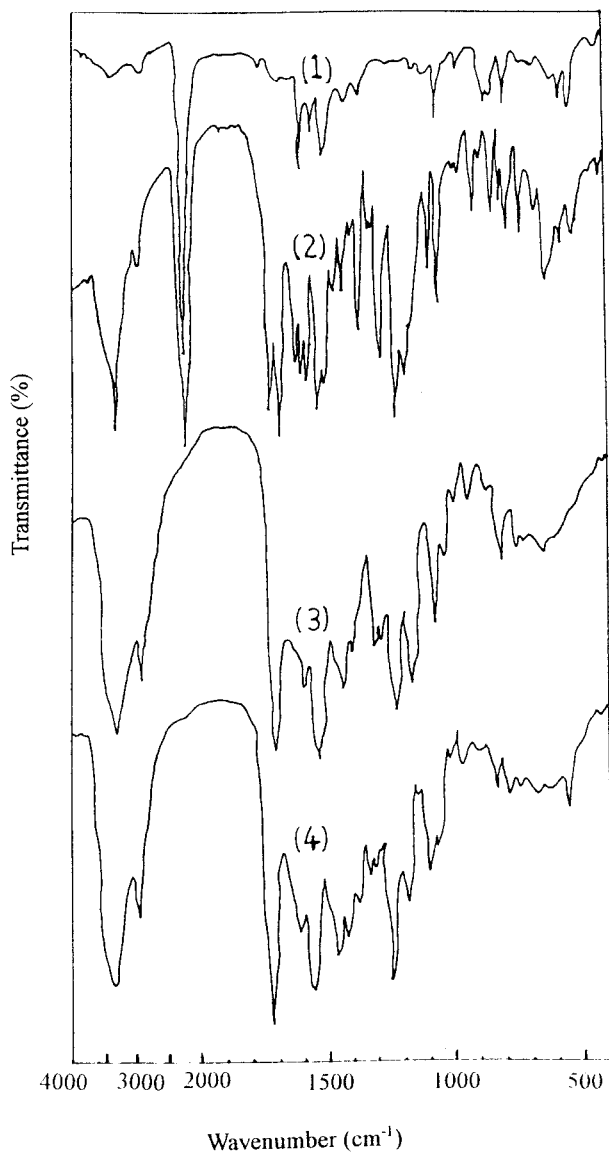
ANAL. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C, 59.21%; H, 5.26%; N, 9.21%. Found: C, 59.31%; H, 5.20%; N, 9.27%.

### Synthesis of Tertiary Amine Urethane Monomer (Second Stage)

In the second stage, the monoadduct was dissolved in THF. An additional inhibitor was added before the blocking agent and the catalyst DBDac. The DMAPA or DMAEA blocking agents were added at one time. The temperature of the reaction was then increased to 45–50°C for 6 h, and the reaction solution was then precipitated by adding *n*-hexane. The flask was then placed in a refrigerator for 1 day to crystallize. The orange–red or white solid monomers were washed and dried in the same way as was their *para*-isomer-blocked monomer. To purify the monomers, further recrystallization was carried out in the THF/*n*-hexane mixtures. Then, the adduct was washed in petroleum ether on a suction funnel and dried in a vacuum oven at 30°C for 1 day. The product was analyzed by elemental analysis, NMR, and IR spectroscopy. Yields were 80.2 and 70.6%, and melting points were 92 and 96°C for DMAPA/HEMA-blocked TDI (DPHT) and DMAEA/HEMA-blocked TDI (DEHT) monomers, respectively [see Scheme 1(B,C)].



**Scheme 3** Crosslinking reaction of TDI with DMAPA.



**Figure 1** IR spectra of (1) TDI, (2) HEMA-blocked TDI, (3) DMAPA/HEMA-blocked TDI, and (4) DMAEA/HEMA-blocked TDI.

ANAL. Calcd for DPHT ( $C_{20}H_{30}N_4O_5$ ): C, 59.11%; H, 7.39%; N, 13.79%. Found: C, 58.67%; H, 7.29%; N, 13.39%. Calcd for DEHT ( $C_{17}H_{27}N_3O_6$ ): C, 58.02%; H, 6.87%; N, 10.69%. Found: C, 57.83%; H, 6.60%; N, 10.42%.

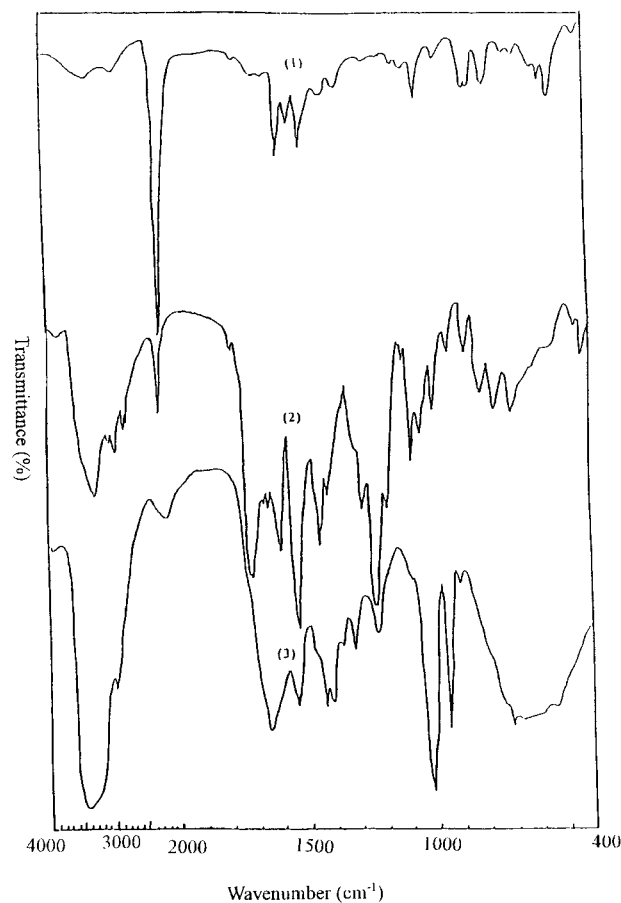
#### Synthesis of Sulfobetaine Monomers

A 100-mL flask equipped with a stirrer, a condenser, and a thermometer was charged with the solvent DMSO and a tertiary amine urethane. To this, PS, dissolved in a small amount of solvent (DMSO), was added dropwise over 1 h. The mix-

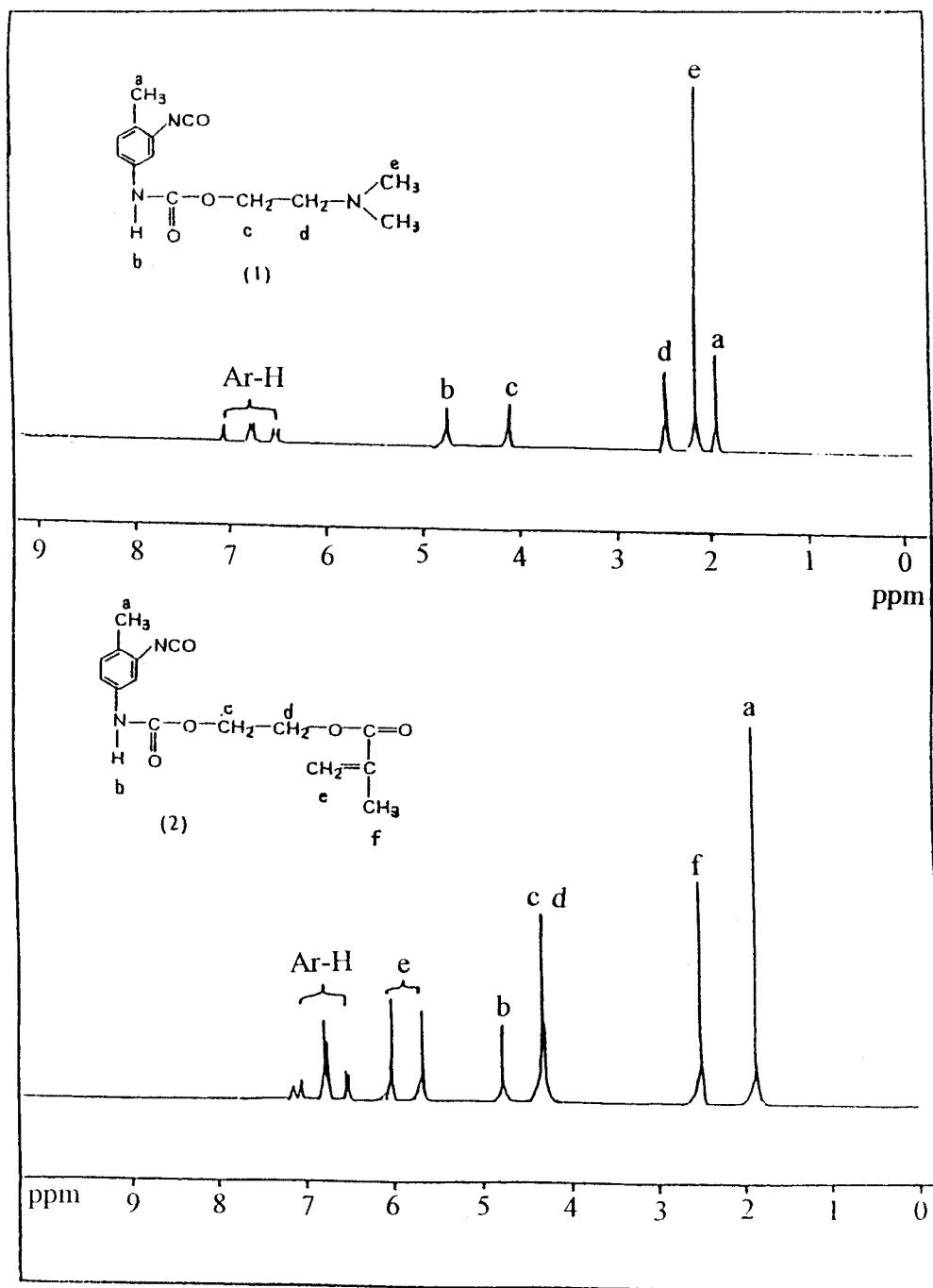
ture was stirred at 0°C in an ice bath for 8 h and left to stand at 25°C for 7 days. Then, the reaction solution was precipitated by adding methyl ethyl ketone (MEK) and washed with THF several times. The solid was collected by filtration and dried under reduced pressure for 24 h to obtain the sulfobetaine monomer. The reactions for the preparation of the two novel sulfobetaines are illustrated in Scheme 2(A,B). The yields of PS/DMAPA/HEMA-blocked TDI (DPHTPS) and PS/DMAEA/HEMA-blocked TDI (DEHTPS) were 68.0 and 91%, respectively. The colors of these sulfobetaines were orange and yellow for DPHTPS and DEHTPS, respectively.

ANAL. Calcd for DPHTPS ( $C_{23}H_{36}N_4O_8$ ): C, 52.27%; H, 6.82%; N, 10.61%. Found: C, 48.46%; H, 7.03%; N, 9.72%. Calcd for DEHTPS ( $C_{22}H_{33}N_3O_9$ ): C, 51.26%; H, 6.42%; N, 8.16%. Found: C, 49.09%; H, 6.58%; N, 7.87%.

The observed data for % C and % N for the two novel sulfobetaines are lower than are the theo-



**Figure 2** IR spectra of (1) TDI, (2) DMAEA-blocked TDI, and (3) DMAPA-blocked TDI.

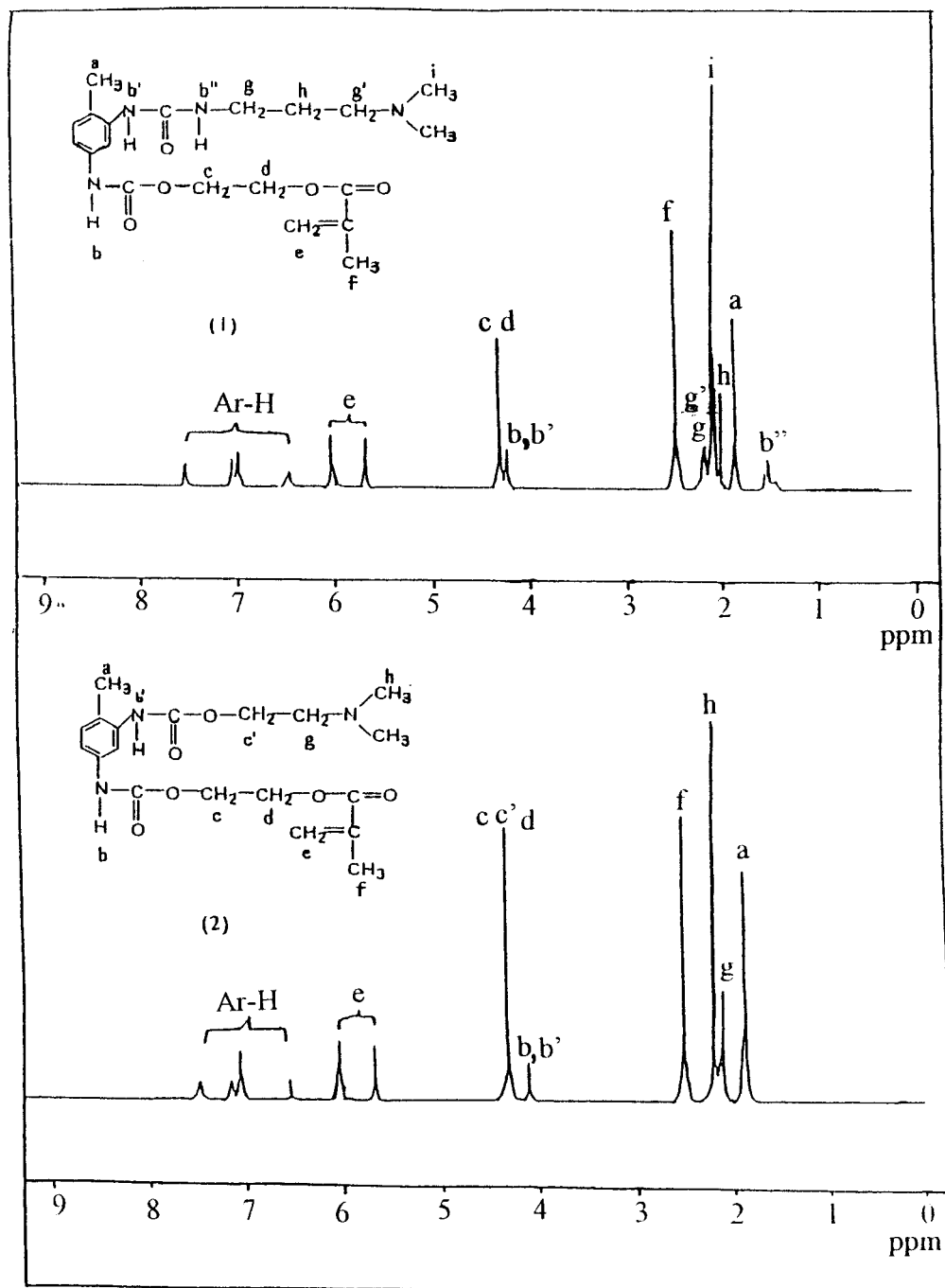


**Figure 3**  $^1\text{H-NMR}$  spectra of (1) DMAEA-blocked TDI and (2) HEMA-blocked TDI.

retical values. This can be explained by the hygroscopicity of the sulfobetaines. To minimize this problem, we calculated the ratio of C/N for each sulfobetaine. The C/N ratio is 4.93 in theory and 4.98 experimentally for DPHTPS and 6.28 in theory and 6.24 experimentally for DEHTPS. This shows good agreement between the experimental and the theoretical values.

#### Polymerization of Sulfobetaine Monomer

The monomer DPHTPS or DEHTPS in the DMSO solution and benzoyl peroxide (BPO) (1 mol %) was charged into an ampule, which was evacuated several times on a high-vacuum system (2 Pa) and sealed off. The ampule was placed in a water bath at  $^{\circ}\text{C}$  for 8 h. The polymer product was



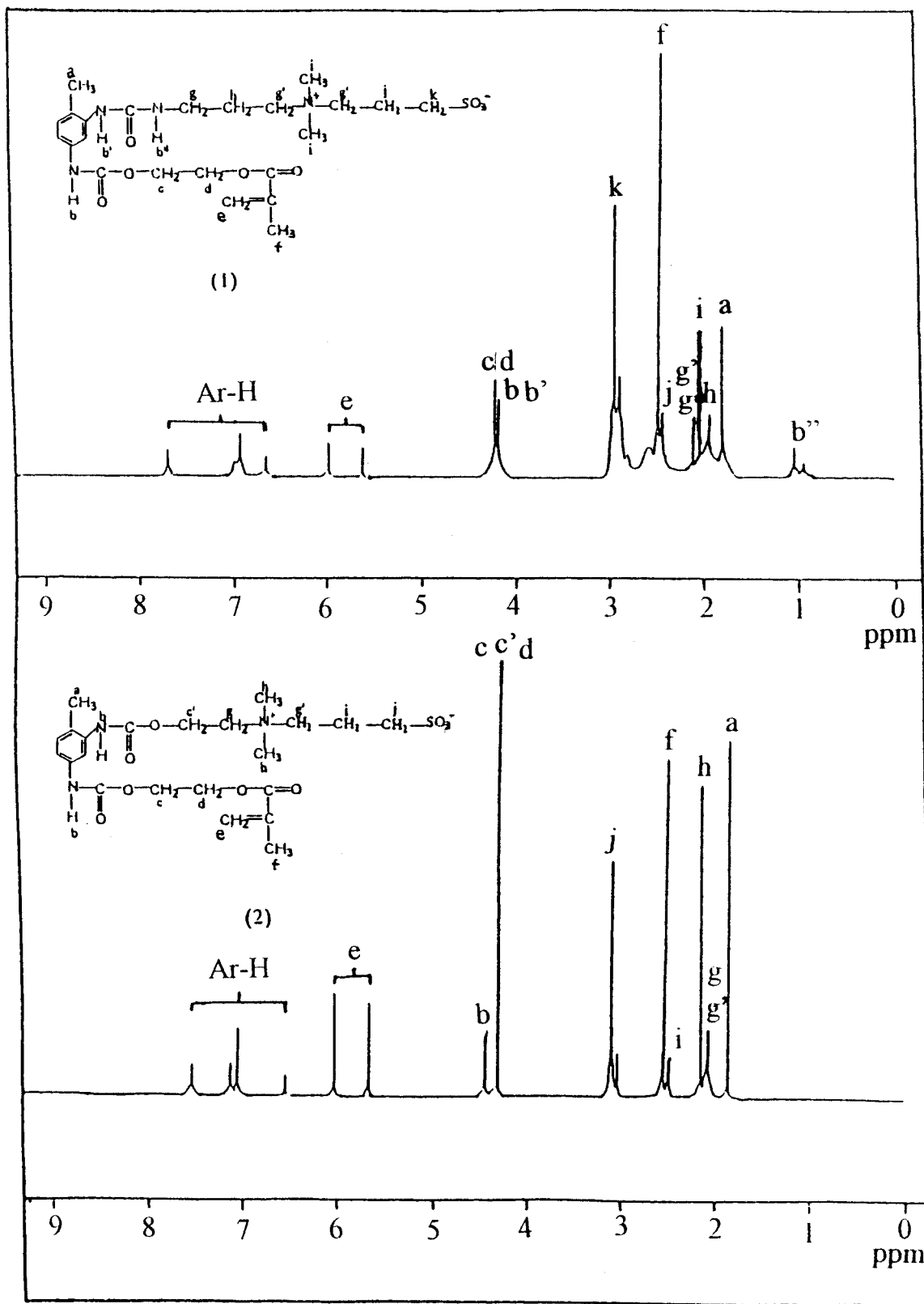
**Figure 4**  $^1\text{H-NMR}$  spectra of (1) DMAPA/HEMA-blocked TDI and (2) DMAEA/HEMA-blocked TDI.

precipitated with methanol, washed with DMSO several times to remove the residual monomer, and dried at  $100^\circ\text{C}$  for 24 h under a vacuum to obtain an orange or yellow solid.

#### Copolymerization of Sulfobetaine Monomer

The monomer DPHTPS or DEHTPS and various monomers such as styrene, acrylamide, methyl

methacrylate (MMA), and HEMA (molar ratio, 1:9, 3:7, and 1:1) in DMSO solution and BPO (1 mol %) were charged into an ampule, which was evacuated several times on a high-vacuum system (2 Pa) and sealed off. The ampule was placed in a water bath at  $60^\circ\text{C}$  for 8 h. The polymer product was precipitated with methanol and washed with the applicable solvent several times



**Figure 5**  $^1\text{H-NMR}$  spectra of (1) PS/PMAPA/HEMA-blocked TDI and (2) PS/DMAEA/HEMA-blocked TDI.



**Table III** Chemical Shifts of  $^1\text{H-NMR}$  for the Various Monomers

Monomer	a	b	c	d	e	f	g	h	i	j	k
HT	1.9	4.8	4.3	4.3	5.7–6.1	2.6					
DPHT	1.8	4.2	4.3	4.3	5.7–6.0	2.5	2.2	2	2.1		
DEHT	1.9	4.1	4.3	4.3	5.6–6.1	2.6	2.1	2.2			
DPHTPS	1.8	4.2	4.3	4.3	5.6–6.0	2.5	2.2	2.0	2.1	2.4	3.0
DEHTPS	1.9	4.4	4.3	4.3	5.7–6.1	2.6	2.1	2.2	2.5	3.1	

to remove the residual monomer and dried at 100°C for 24 h under a vacuum.

## RESULTS AND DISCUSSION

### Characterization

The yields and melting points of the monoadducts, tertiary amine urethanes, and novel sulfo-betaines are listed in Table II. One may note that the yields of the monoadducts are very high and their melting points lower than that for the tertiary amine urethanes. The melting points of the two novel sulfo-betaines cannot be determined, because the sulfo-betaine monomers were hygroscopic and typically polymerized or decomposed upon melting.

### Reaction of TDI with HEMA, DMAPA, and DMAEA

As described above, the preparations were done via a two-stage method. The first-stage reaction of

HEMA with TDI in petroleum ether was performed and the intermediate product was precipitated out of solution. The heterogeneous first-stage reaction has the merit of reducing the formation of diadduct (product from the reaction of both isocyanate groups of TDI with HEMA). Before this method was adopted, several trials were run with both reaction stages run homogeneously or heterogeneously, but none was satisfactory because they either formed too much diadduct or too sticky a product. For example, TDI reacted with DMAPA to form a gel and TDI reacted with DMAEA to form a sticky product. Hence, the two-stage reaction of DMAPA-blocked TDI and DMAEA-blocked TDI was not finished. The gelation of TDI with DMAPA is shown in Scheme 3, when both isocyanate groups of TDI react with the diamine group of DMAPA.

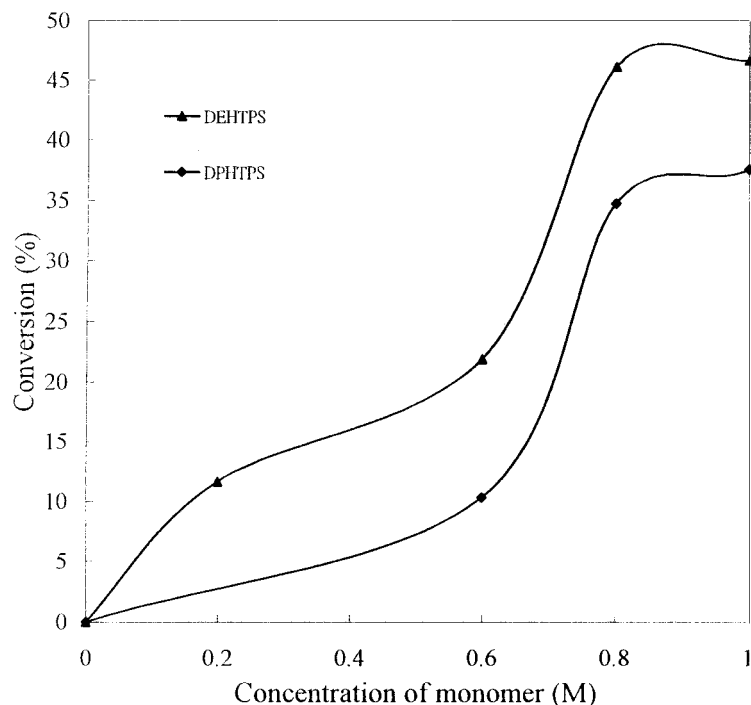
### IR Spectra Analysis

IR spectra were recorded on a Jasco FTIR 7000 spectrometer operating at 400–4000  $\text{cm}^{-1}$  at

**Table IV** Solubilities of the Novel Sulfo-betaines in Various Solvents

Solvent	HT	DPHT	DEHT	DPHTPS	DEHTPS	Poly(DPHTPS)	Poly(DEHTPS)
H <sub>2</sub> O	X	X	X	O	O	X	X
Acetone	X	X	X	X	X	X	X
MEK	X	X	X	X	X	X	X
CH <sub>3</sub> OH	O	X	X	X	X	X	X
C <sub>2</sub> H <sub>5</sub> OH	O	X	X	X	X	X	X
iso-C <sub>3</sub> H <sub>7</sub> OH	X	X	X	X	X	X	X
THF	V	V	V	X	X	X	X
DMSO	V	V	V	V	V	X	X
DMF	V	V	V	V	V	X	X
DMAc	V	V	V	V	V	X	X
Toluene	X	X	X	X	X	X	X
Petroleum ether	X	X	X	X	X	X	X
CHCl <sub>3</sub>	X	X	X	X	X	X	X
Ethyl acetate	V	X	X	X	X	X	X
CCl <sub>4</sub>	X	X	X	X	X	X	X
CH <sub>3</sub> CN	X	X	X	X	X	X	X
<i>n</i> -Hexane	X	X	X	X	X	X	X

V, soluble; O, slightly soluble; X, insoluble.



**Figure 6** Conversion of polymerization as a function of concentration of DEHTPS at 60°C for 8 h.

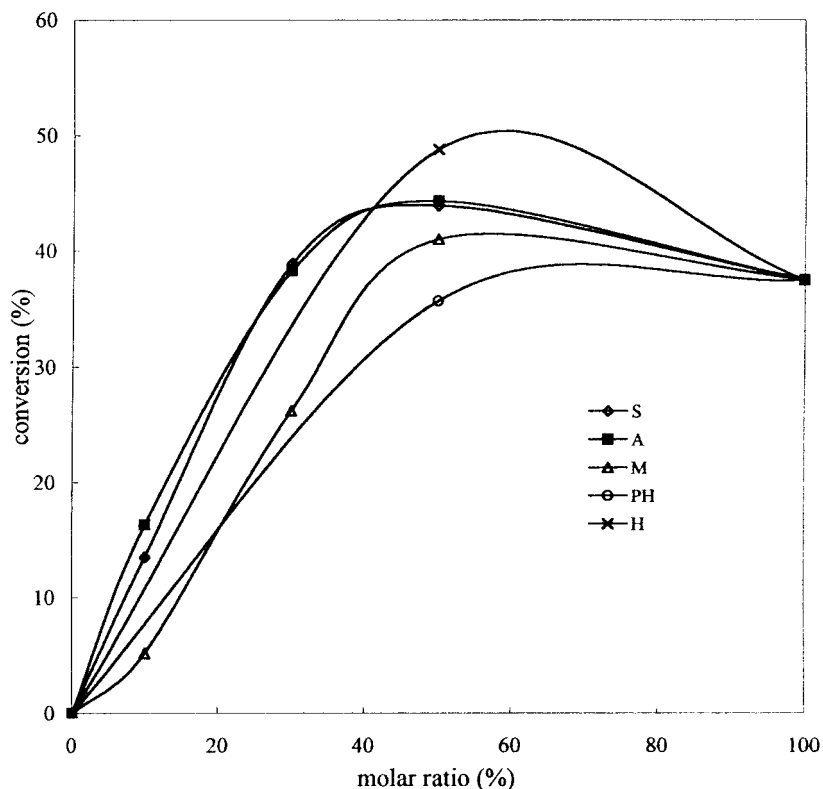
room temperature. The IR spectra of TDI, HEMA-blocked TDI, and DMAPA and DMAEA/HEMA-blocked TDI are shown in Figure 1. The characteristic absorption peaks for HEMA at 3300, 1700, 1645, and 1410  $\text{cm}^{-1}$  are present in the HEMA-blocked TDI. The characteristic absorption of an isocyanate functional group is at 2240–2275  $\text{cm}^{-1}$ , which gradually decreases from TDI, HEMA-blocked TDI, to DMAPA/HEMA-blocked TDI. This indicates that HEMA reacts with the *para*-isocyanate group of TDI in the first stage and then DMAPA reacts with the *ortho*-isocyanate of TDI in the second stage. Since the *para*-isocyanate groups are eight to ten times more reactive than is the *ortho* group, HEMA would preferentially react with *para*-isocyanate.<sup>24–26</sup> (HEMA is the part of the monomer that will be used for polymerization.)

The IR spectrum of DMAEA/HEMA-blocked TDI in Figure 1(4) exhibits a similar tendency to Figure 1(3). Hence, the formed monoadduct (DMAPA/HEMA-blocked TDI) and DMAEA/HEMA-blocked TDI can be easily produced by the two-stage method. Figure 2 shows IR spectra of TDI, DMAEA-blocked TDI, and DMAPA-blocked TDI. The characteristic absorption of an isocyanate functional group disappeared in DMAPA-blocked TDI. This implies that DMAPA reacts

with both isocyanate groups of TDI. This result confirms the gelation of TDI with DMAPA. The characteristic absorption of an isocyanate group of DMAEA-blocked TDI was diminished. The isocyanate peak of DMAEA-blocked TDI is smaller than that of HEMA-blocked TDI. This implies that the residual isocyanate group of DMAEA-blocked TDI is smaller than that of HEMA-blocked TDI. The characteristic IR absorption peaks for urethane at 3400  $\text{cm}^{-1}$  are present in each blocked TDI monomer. The IR spectra of two novel sulfobetaines were not found, because the sulfobetaine monomers are hygroscopic and their KBr pellets could not be formed.

#### <sup>1</sup>H-NMR Spectra Analysis

NMR spectra were measured with a JEOL 100 spectrometer operating at 500 MHz for <sup>1</sup>H at 300 K. The samples were dissolved in DMSO-*d*<sub>6</sub>. The <sup>1</sup>H-NMR spectra shown in Figure 3 also provide good evidence that the materials prepared are DMAEA- and HEMA-blocked TDI. The <sup>1</sup>H-NMR spectra shown in Figure 4 indicate that the tertiary amine urethanes, DMAPA/HEMA-blocked TDI and DMAEA/HEMA-blocked TDI, are the monomers expected. The two peaks at 5.8–6.2 ppm are characteristic of the vinyl peak for the



**Figure 7** Conversion of DPHTPS copolymerized with S (styrene), A (acrylamide), M (MMA), PH (DPHT), and H (HEMA) monomers as a function of molar ratio at 60°C for 8 h.

blocked monomer. The  $^1\text{H-NMR}$  spectra of the two novel sulfobetaines shown in Figure 5 indicate that the methylene groups neighboring the sulfonate group appear at 3.0 ppm. The analysis of the  $^1\text{H-NMR}$  for each compound is determined using the step-by-step method. According to this method, we can easily assign every peak in the  $^1\text{H-NMR}$  spectra. The chemical shifts for the various compounds are listed in Table III.

#### Solubility of the Blocked Adducts and Two Novel Sulfobetines

The solubility characteristic of the blocked monomers, DPHT and DEHT, are listed in Table IV. The results indicate that the blocked monomers could only dissolve in strongly polar organic solvents, such as DMSO, DMAc, DMF, and THF.

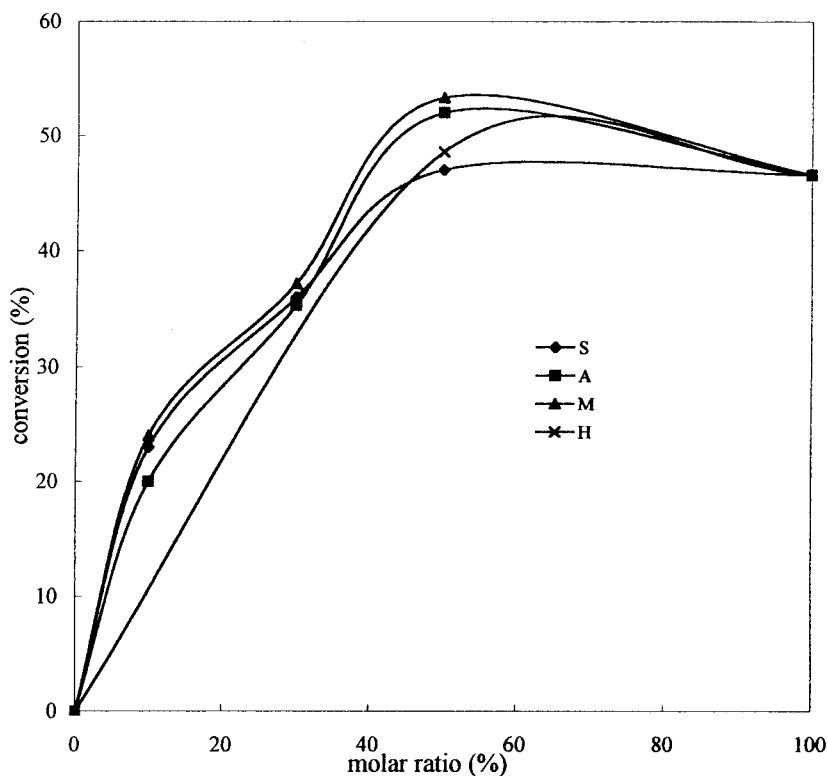
The solubilities of the two novel sulfobetaines monomers and polymers shown in Table IV indicate that the sulfobetaine monomers can dissolve in strongly polar organic solvents, such as DMSO, DMAc, and DMF, but these polymers cannot dissolve in the corresponding solvents.

#### Effect of Monomer Concentration on Polymerization Conversion

The polymerization conversion of the DEHTPS monomer in DMSO at 60°C for 8 h shown in Figure 6 increased with an increasing concentration of the monomer. But the conversion was only 46% in 1.0M. Thus, compared with poly(DMAAPS),<sup>12</sup> the polymerization conversion of DEHTPS is lower. This result indicates that DEHTPS is not easily polymerized.

The polymerization conversion of the DPHTS monomer in DMSO at 60°C for 8 h increased with increasing monomer concentration. But the conversion was only 37% in 1.0M. Compared with poly(DEHTPS), the polymerization conversion of DPHTS is too low. This result also indicates that DPHTPS is not easily polymerized under these conditions.

From the above results, it can be concluded that the homopolymerization rate of these two sulfobetaine monomers is low. This may be due to their low solubility in DMSO and precipitation.



**Figure 8** Conversion of DEHTPS copolymerized with S (styrene), A (acrylamide), M (MMA), and H (HEMA) monomers as a function of molar ratio at 60°C for 8 h.

#### Effect of Various Monomers on the Conversion

The copolymerization was carried out at various molar ratios (1:9, 3:7, and 5:5) of DPHTPS and different comonomers. The conversion in the copolymerization of DPHTPS with styrene, acrylamide, MMA, and HEMA in DMSO at 60°C after 8 h, and shown in Figure 7, increased at increasing DPHTPS concentration. When the molar ratio reaches 5:5, the conversion is highest. This conversion approaches that for the homopolymerization of DPHTPS (see Fig. 7).

The conversion in the copolymerization of DEHTPS with styrene, acrylamide, MMA, and HEMA in DMSO at 60°C after 8 h is shown in Figure 8. The results are similar to those for the DPHTPS series.

#### CONCLUSIONS

A two-stage method for preparing novel sulfobetaines was designed. The first-stage reaction of TDI with HEMA was carried out in petroleum ether with precipitation from the reaction solution. The second-stage reaction of the monoadduct

with the blocking agent, DMAPA or DMAEA, was homogeneously carried out in THF to form the tertiary amine urethanes. The two novel sulfobetaines were then derived from these two tertiary amine urethanes for reaction with PS. The solubility of these products is good in strongly polar organic solvents.

The polymerization and copolymerization conversion for these two novel sulfobetaines is low. This may be due to their low solubility and precipitation in DMSO.

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