Hydrogen-Transfer Polymerization of Vinyl Monomers Derived from *p*-Tolylsulfonyl Isocyanate and Acrylamide Derivatives

Takeru Iwamura, Ikuyoshi Tomita,† Masato Suzuki,†† and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8503

†Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8502

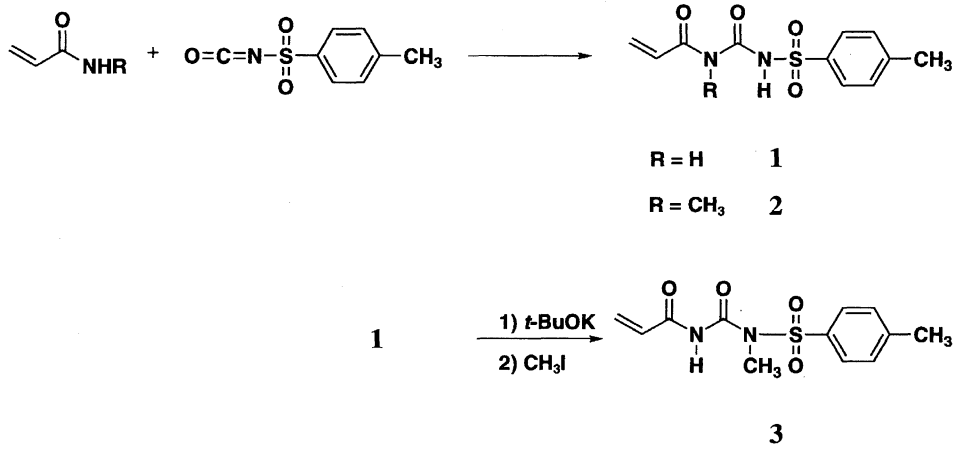
††Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552

(Received November 11, 1997)

The hydrogen-transfer polymerization of *N*-acryloyl-*N'*-*p*-tolylsulfonylurea (**1**) prepared by the reaction of *p*-tolylsulfonyl isocyanate with acrylamide, was carried out at 80 °C for 24 h in *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), and toluene containing *N*-phenyl-2-naphthylamine (1 mol%) as a radical inhibitor using *t*-BuOK or 1,3-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 mol%) as an initiator. Polymers obtained by *t*-BuOK in polar solvents were composed of the hydrogen-transfer polymerization unit selectively, while those afforded by *t*-BuOK in less polar solvents or by DBU were composed of both the hydrogen-transfer and the vinyl polymerization units. Although *N*-acryloyl-*N*-methyl-*N'*-*p*-tolylsulfonylurea (**2**) prepared by the reaction of *p*-tolylsulfonyl isocyanate with *N*-methylacrylamide, gave low molecular-weight compounds (**6**—**8**) via the generation of the sulfonyl isocyanate, *N*-acryloyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea (**3**) underwent the selective hydrogen-transfer polymerization.

Activated isocyanates such as *N*-acyl isocyanates and *N*-sulfonyl isocyanates are known to be much more reactive toward nucleophiles than common isocyanates. For example, sulfonyl isocyanates readily react with various weak nucleophiles such as amides under mild conditions without any catalysts to afford the corresponding adducts.[1—3] We have developed the syntheses of novel polymers based on *N*-acyl isocyanates and *N*-sulfonyl isocyanates.[4—9] For instance, poly(*N*-acryloyl-*N'*-*p*-tolylsulfonylurea) have been prepared by the radical polymerization of *N*-acryloyl-*N'*-*p*-tolylsulfonylurea (**1**) (an adduct prepared easily from acrylamide and *p*-tolylsulfonyl isocyanate).[9] The resulting polymer has the –CO–NH–CO–NH–SO_2– repeating unit in the side chain and has been demonstrated to exhibit a unique hydrolytic character.

Since monomer **1** has two acidic protons on the nitrogen atoms, its anionic polymerization may involve the hydrogen-transfer process reported previously for acrylamide, methacrylamide, α-substituted acrylamide, β-substituted acrylamide, *N*-substituted acrylamide, etc.[10—14] Based on the characteristics of the hydrogen-transfer polymerization, unique functional groups (i.e., –CO–N (CONHTs)– or



Scheme 1.

–CO–NH–CO–N(Ts)–) may be incorporated into the main chain of the polymers produced. Accordingly, we communicated briefly on the hydrogen-transfer polymerization of **1** with *t*-BuOK or DBU as an initiator in DMF.[15] The polymer obtained by *t*-BuOK in DMF was found to be composed of the selective hydrogen-transfer polymerization unit, while those afforded by DBU in DMF was composed of both the hydrogen-transfer and the vinyl polymerization units. In order to clarify solvent and initiator effects on the hydrogen-transfer polymerization of **1** and to understand the contribution of the two active hydrogens with different acidities, we wish to describe here the detailed anionic polymerization behavior of **1** and that of monomers (**2** and **3**) in which either one of the two active hydrogens of **1** is masked with a methyl group (Scheme 1).

Experimental

Materials. 1,3-Diazabicyclo[5.4.0]undec-7-ene (DBU), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile (MeCN) were dried over CaH_2, distilled, and stored under nitrogen. Toluene was dried over sodium metal and distilled under nitrogen. Potassium *t*-butoxide (*t*-BuOK) was prepared from *t*-butyl alcohol and potassium. *N*-Acryloyl-*N'*-*p*-tolylsulfonylurea (**1**) was prepared by our reported procedure.[9] Other commercially available reagents were used without further purification.

Measurements. IR spectra were measured on a JASCO FT/IR-5300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX90 (^{1}H NMR: 90 MHz, ^{13}C NMR: 22.4 MHz) or a JEOL JNM-EX400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) spectrometer.

Number- ($\overline{M}_n$) and weight-average $\overline{M}_w$) molecular weights and molecular weight distributions ($\overline{M}_w/\overline{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh Co. HLC-8020 system equipped with polystyrene gel columns (TSK® gel G6000HXL, TSK® gel G5000HXL, TSK® gel G4000HXL, and TSK® gel G2500HXL) using DMF containing LiBr (5.8 mM) as eluent, a flow rate of 1.0 mL min^{-1}, polystyrene calibration, and an ultraviolet (UV) detector.

Fast atom bombardment mass spectra (FAB/MS) were recorded by using a JEOL JMS-700 spectrometer, whereby a mixture of a sample and *m*-nitrobenzyl alcohol on a standard FAB target was subjected to a beam of xenon atoms produced at 6 keV, 2 mA.

Synthesis of *N*-Acryloyl-*N*-methyl-*N'*-*p*-tolylsulfonylurea (2). To a 20 mL round-bottomed flask containing a benzene (8 mL) solution of *p*-tolylsulfonyl isocyanate (1.40 g, 7.09 mmol) was added *N*-methylacrylamide (0.59 g, 6.88 mmol). The mixture was stirred at room temperature for 29 h, subsequently heated at 40 °C for 4 h under nitrogen. The resulting mixture was evaporated to dryness and the residue was purified by chromatography on silica gel with chloroform as eluent to isolate the *N*-methylated monomer **2**, which was further purified by recrystallization from benzene. Yield 87% (1.69 g, 5.99 mmol), mp 110.0—110.5 °C. IR (KBr) 3414 (NH), 1715 (C=O), 1664 (C=O) 1618 (C=C), 1449 (–CH_2–), 1358 (–SO_2–), 1175 (–SO_2–), 548 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$, 90 MHz) δ = 2.44 (s, 3H, CH_3– C_6H_4–), 3.26 (s, 3H, CH_3–N–), 5.97 (dd, J = 7.61 and 4.32 Hz, 1H, CH_2=C*H*–), 6.58 (d, J = 4.32 Hz, 1H, CH_2=CH– *cis*), 6.60 (d, J = 7.61 Hz, 1H, CH_2=CH– *trans*), 7.33 (d, J = 8.37 Hz, 2H, C_6H_4), 7.98 (d, J = 8.37 Hz, 2H, C_6H_4), 12.11 (bs, 1H, –CON*H*SO_2–); ^{13}C NMR (DMSO-d_6, 22.4 MHz) δ = 21.2, 31.2, 127.5, 128.7, 129.5, 133.8, 135.9, 144.8, 150.1, 170.0. Found: C, 50.99; H, 4.96; N, 9.87; S, 11.30%. Calcd for $C_{12}H_{14}N_2O_4S$: C, 51.05; H, 5.00; N, 9.92; S, 11.36%.

Synthesis of *N*-Acryloyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea (3). To a 100 mL round-bottomed flask containing a DMF (20 mL) solution of *t*-BuOK (2.03 g, 18.09 mmol) and *N*-phenyl-2-naphthylamine (65.4 mg, 0.30 mmol) was added **1** (5.27 g, 19.64 mol) under nitrogen. After the mixture was stirred at room temperature for 15 h, methyl iodide (5.68 g, 40.02 mmol) was added and the mixture was stirred at ambient temperature for 5 d. The resulting mixture was treated with water and extracted with chloroform. The organic phase was washed with water three times, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by chromatography on silica gel with chloroform as eluent to isolate the *N'*-methylated monomer **3**, which was further purified by recrystallization from hexane–chloroform. Yield 45% (2.48 g, 8.78 mmol), mp 85—86 °C. IR (KBr) 3410 (NH), 3113 (C=C), 1725 (C=O), 1694 (C=O), 1630 (C=C), 1460 (–CH_2–), 1356 (–SO_2–), 1152 (–SO_2–), 546 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$, 90 MHz) δ = 2.46 (s, 3H, CH_3–C_6N_4–), 3.16 (s, 3H, CH_3–N–), 5.89 (dd, J = 9.60 and 2.00 Hz, 1H, CH_2=CH– *trans*), 6.46 (dd, J = 19.60 and 2.00 Hz, 1H, CH_2=CH– *cis*), 6.80 (dd, J = 19.60 and 9.60 Hz, 1H, CH_2=C*H*–), 7.37 (d, J = 8.30 Hz, 2H, C_6H_4), 7.74 (d, J = 8.30 Hz, 2H, C_6H_4), 10.13 (bs, 1H, –CON*H*CO–); ^{13}C NMR (DMSO-d_6, 22.4 MHz) δ = 21.6, 32.4, 127.1 129.9, 130.4, 131.0, 134.3, 145.9, 148.8, 164.7. Found: C, 50.99; H, 4.96; N, 9.86; S, 11.12%. Calcd for $C_{12}H_{14}N_2O_4S$: C, 51.05; H, 5.00; N, 9.92; S, 11.36%.

Synthesis of Potassium Salt of 1. To a 100 mL round-bottomed flask containing an acetonitrile (20 mL) solution of *t*-BuOK (0.21 g, 1.87 mmol) was added **1** (0.50 g, 1.86 mmol) under nitrogen. After the mixture was stirred at room temperature for 24 h, the resulting suspension was evaporated to dryness to give an essentially pure form of the potassium salt. IR (KBr) 3451 (NH), 1716 (C=O), 1664 (C=O), 1624 (C=C), 1321 (–SO_2–), 1142 (–SO_2–), 556 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.46 (s, 3H, CH_3–C_6H_4–), 5.89 (d, J = 10.80 Hz, 1H, CH_2=CH– *cis*), 6.49 (d, J = 17.20 Hz, 1H, CH_2=CH– *trans*), 6.76 (dd, J = 10.80 and 17.20 Hz, 1H, CH_2=C*H*–), 7.38 (d, J = 8.00 Hz, 2H, C_6H_4), 7.73 (d, J = 8.00 Hz, 2H, C_6H_4), 10.14 (s, 1H, –CON*H*CO–).

Hydrogen-Transfer Polymerization (Typical Procedure). The monomer (**1**, **2**, or **3**) (1.0 M, 1 M = 1 mol dm^{-3}), *t*-BuOK or DBU (3 mol%), and *N*-phenyl-2-naphthylamine (1 mol%, an inhibitor for radical polymerization) were dissolved in DMF, DMSO, MeCN, or toluene in a test tube under nitrogen atmosphere. After heating at 80 °C for 24 h, the resulting mixture was poured into diethyl ether and the isolated polymer was dried in vacuo.

Polymer 4 Obtained from 1 (Run 1 in Table 1). Yield 10%; IR (KBr) 3436 (NH), 2924 (–CH_2–), 2855 (–CH_2–), 1769 (C=O), 1692 (C=O), 1476 (–CH_2–), 1383 (–SO_2–), 1159 (–SO_2–), 766 (–CH_2–), 550 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$/ CF_3COOH 4/1 v/v, 400 MHz) δ = 2.46 (s, 3H×0.9, CH_3–C_6H_4–), 2.72—3.07 (m, 2H, –CH_2CH_2–CO–), 3.23—4.37 (m, 2H, –N–CH_2–CH_2–), 7.27—7.48 (m, 2H×0.9, CH_3–C_6H_4–), 7.60—7.80 (m, 2H×0.47, –C_6H_4–SO_2– in *x* unit), 7.80—7.97 (m, 2H×0.43, –C_6H_4–SO_2– in *y* unit), 10.48 (bs, 1H, –CON*H*CO–); ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 21.0, 30.9, 31.4, 34.8, 35.9, 36.8, 37.7, 40.7, 125.5, 126.5, 128.0, 129.6, 135.3, 137.3, 142.7, 144.8, 145.8, 148.6, 149.6, 150.0, 168.9, 172.8.

Polymer 4 Obtained from 1 (Run 5 in Table 1). Yield 9%; IR (KBr) 3449 (NH), 2928 (–CH_2–), 2857 (–CH_2–), 1769 (C=O), 1701 (C=O), 1451 (–CH_2–), 1352 (–SO_2–), 1161 (–SO_2–), 764 (–CH_2–), 550 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$/ CF_3COOH 4/1 v/v, 400 MHz) δ = 1.00—2.74 (m, 3H, –CH_2–C*H*–), 2.46 (s, 3H×0.94,

Table 1. Hydrogen-Transfer Polymerization of *N*-Acryloyl-*N'*-*p*-tolylsulfonylurea (**1**)[a]

Run	Initiator	Solvent	Conv. (%)[b]	Yield (%)[c]	$\overline{M}_n$	$(\overline{M}_w/\overline{M}_n)$[d]	*x*/*y*/*z*[b]
1	*t*-BuOK	DMF	75	10	4300	(1.07)	52/48/0
2	*t*-BuOK[e]	DMF	100	39	4700	(1.18)	8/21/71
3	*t*-BuOK	DMSO	69	18	3100	(1.38)	61/36/0
4	*t*-BuOK	MeCN	84	10	5200	(1.13)	32/41/27
5	*t*-BuOK	PhMe	31	9	3200	(1.20)	3/3/94
6	DBU	DMF	95	25	3700	(1.37)	36/41/23
7	DBU	DMSO	89	36	3600	(1.28)	42/28/30
8	DBU	MeCN	87	26	4300	(1.13)	30/39/31
9	DBU	PhMe	97	30	3600	(1.11)	30/41/29

a) Conditions: [**1**] = 1 M, initiator (3 mol% unless otherwise noted), *N*-phenyl-2-naphthylamine (1 mol%), 80 °C, 24 h. b) Determined by ^{1}H NMR spectra. c) Diethyl ether-insoluble part. d) Estimated by GPC, based on polystyrene standards, eluent: DMF containing LiBr (5.8 mM). e) Initiator (300 mol%).

CH_3–C_6H_4–), 2.72—3.07 (m, 2H×0.07, –CH_2–CH_2–CO–), 3.23—4.37 (m, 2H×0.07, –N–CH_2–CH_2–). 7.00—7.64 (m, 2H, CH_3–C_6H_4–), 7.64—7.82 (m, 2H×0.03, –C_6H_4–SO_2– in *x* unit), 7.70—8.20 (m, 2H×0.97, –C_6H_4–SO_2 in *y* and *z* unit), 9.70 (bs, 1H×0.55H, –CONHCO–); ^{13}C NMR (DMSO-d_6, 100 MHz), δ = 21.0, 30.9, 33.8, 34.9, 36.0, 44.7, 125.6, 126.5, 127.7, 129.3, 135.3, 137.2, 141.3, 141.9, 144.6, 167.8, 170.3.

Polymer 9 Obtained from 3 (Run 3 in Table 2). Yield 14%; IR (KBr) 3449 (NH), 2961 (–CH_2–), 2926 (–CH_2–), 1746 (C=O), 1701 (C=O), 1458 (–CH_2–), 1366 (–SO_2–), 1165 (–SO_2–), 756 (–CH_2–), 548 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$/ CF_3COOH 4/1 v/v, 400 MHz) δ = 2.46 (s, 3H, CH_3–C_6H_4–), 2.55—3.55 (m, 5H, –N–CH_3, and –CH_2–CH_2–CO–), 3.60—4.50 (m, 2H, –N–CH_2–CH_2–), 7.27—7.50 (m, 2H, CH_3–C_6H_4–), 7.50—7.90 (m, 2H, –C_6H_4–SO_2–); ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 21.0, 32.8, 34.3, 37.8, 45.3, 46.8, 126.7, 127.3, 128.3, 129.7, 130.4, 133.8, 136.2, 142.6, 143.4, 146.0, 164.5, 171.6.

Results and Discussion

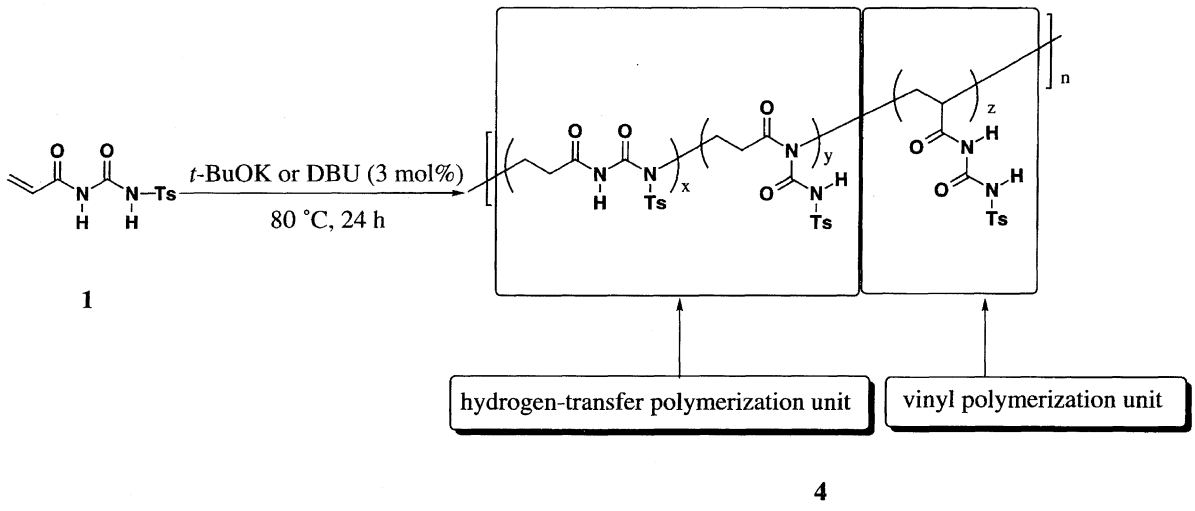
Hydrogen-Transfer Polymerization of 1. The polymerization of **1** was carried out at 80 °C for 24 h using *t*-BuOK (3 mol%) as an initiator in various solvents containing *N*-phenyl-2-naphthylamine (1 mol%) as a radical polymerization inhibitor (Scheme 2). As a result, polymer **4** was obtained in 9—18% yield as a diethyl ether-insoluble part (Table 1, Runs 1 and 3—5). ^{1}H NMR spectra of the obtained polymers support the conclusion that the hydrogen-transfer polymerization proceeded selectively in DMF and DMSO (Runs 1 and 3), while both the hydrogen-transfer and the vinyl polymerization took place in MeCN and toluene (Runs 4 and 5). When the polymerization of **1** was carried out with a large excess amount of *t*-BuOK (300 mol%) as an initiator in DMF, the polymer was obtained in 39% yield. The polymer consisted of 77% of the vinyl polymerization unit and 23% of the hydrogen-transfer unit.

The ^{1}H NMR spectrum of the polymer obtained in Run 1 is shown in Fig. 1a, in which two peaks attributable to the methylene protons adjacent to the nitrogen atom and those adjacent to the carbonyl group were observed at δ = 3.23—4.37 (e, f) and 2.72—3.07 (g, h), respectively. The assignments of the peaks at δ = 7.27—7.98 (b, c) were carried out on the basis of the spectra of model compounds (i.e., *N*-propionyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea and *N*-propionyl-*N*-*n*-butyl-*N'*-*p*-tolysulfonylurea for *x* and *y* units, respectively)[16] and the ratio of *x* to *y* units in Scheme 2 was determined by the integral ratio between these peaks. Because both of two possible hydrogen-transfer units could be observed in the produced polymers, both of the N–H moieties in **1** should participate in the hydrogen-transfer process. In the ^{1} NMR spectrum of the polymer obtained in Run 5 (Fig. 1b), the signals due to the methylene protons (e, f, g, h) of the hydrogen-transfer polymerization unit were negligi-

Table 2. Hydrogen-Transfer Polymerization of *N*-Acryloyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea (**3**)

Run	Initiator	Solvent	Conv. (%)[b]	Yield (%)[c]	$\overline{M}_n$	$(\overline{M}_w/\overline{M}_n)$[d]	*x*/*y*[b]
1	*t*-BuOK	DMF	75	11	7200	(1.51)	100/0
2	*t*-BuOK	DMSO	69	19	5300	(1.86)	100/0
3	*t*-BuOK	MeCN	84	33	8600	(1.42)	100/0
4	*t*-BuOK	PhMe	85	14	9600	(1.75)	100/0
5	DBU	DMF	68	14	9900	(1.39)	55/45
6	DBU	DMSO	97	22	8200	(1.25)	56/44
7	DBU	MeCN	76	28	7700	(1.41)	67/33
8	DBU	PhMe	74	21	7900	(2.09)	61/39

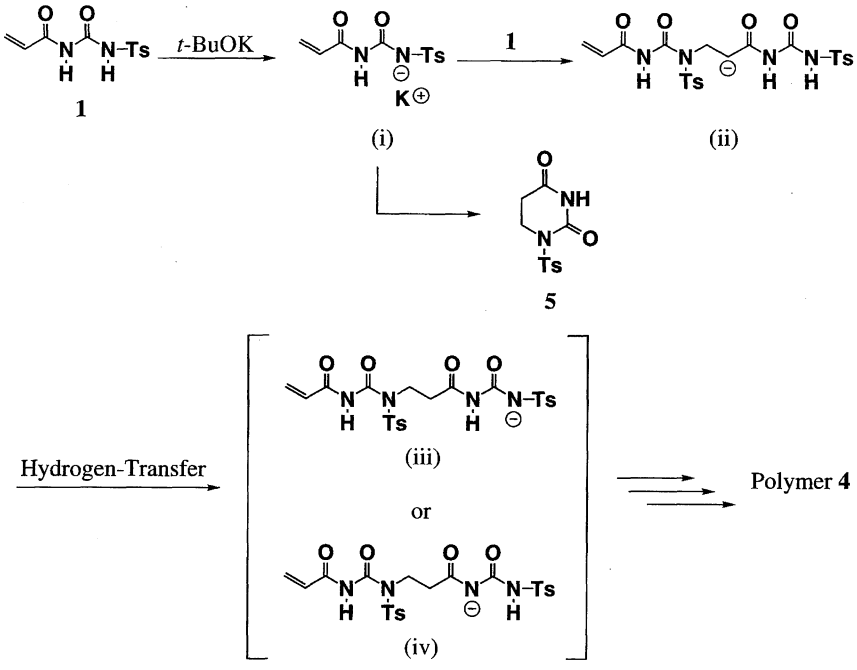
a) Conditions: [**3**] = 1 M, initiator (3 mol%), *N*-phenyl-2-naphthylamine (1mol%), 80 °C, 24 h. b) Determined by ^{1}H NMR spectra. c) Diethyl ether-insoluble part. d) Estimated by GPC, based on polystyrene standards, eluent: DMF containing LiBr (5.8 mM).



Scheme 2.

ble, while those attributable to the methylene protons of the vinyl polymerization unit were observed as major peaks at $\delta = 1.00$—2.74 (j, k). However, in some cases, the peak areas of the aromatic protons were smaller than expected (Table 1: Runs 1—5, by 0—22%).[17] However, low molecular-weight compounds which consisted of the eliminated aromatic parts from the monomer or the polymer were not detected in the diethyl ether-soluble part, while a 6-membered cyclic compound (**5**) was isolated in 30% yield (Scheme 3 and Table 1, Run 3).[18]

As for the initiation process, two possibilities might be speculated: the nucleophilic addition of the initiating anion (t-BuO$^-$) toward the unsaturated bonds in **1** and subsequent transfer of the amide proton or the hydrogen abstraction from the N–H moieties in **1** by t-BuOK. To clarify which process is correct, **1** was reacted with an equimolar amount of t-BuOK at room temperature for 24 h in acetonitrile. The ^{1}H NMR spectrum of the reaction mixture indicated that a potassium salt of **1**, i.e., CH_2=CHCONHCON$^-$TsK$^+$, was produced almost quantitatively by deprotonation with t-BuOK. When the hydrogen-transfer polymerization of **1** was carried out at 80 °C for 24 h using the potassium salt of **1** (3 mol%) as an initiator, the polymer having the same structure as that prepared by t-BuOK was obtained. Therefore, the polymerization most probably proceeds via the potassium salt (i) (Scheme 3). In the propagation process, hydrogens of NH groups may transfer to the anion (ii) generated by the nucleophilic attack of (i) to the β-carbon of **1** to form two kinds of N-anions ((iii) and (iv)) and the hydrogen-transfer polymerization units should be produced by the nucleophilic attack



Scheme 3.

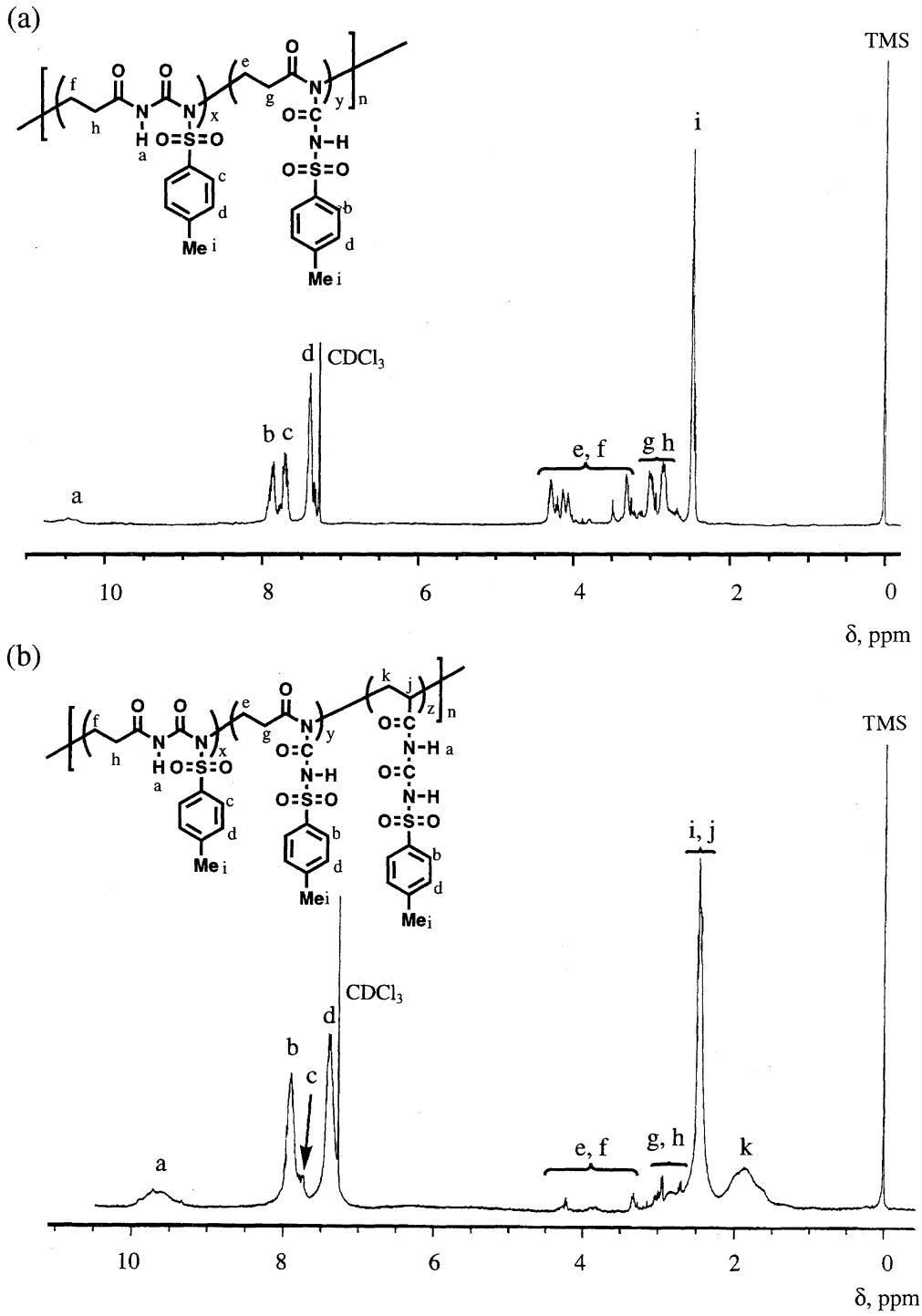


Fig. 1. ^{1}H NMR spectra ($CDCl_3/CF_3COOH$) of **4** prepared in Run 1 of Table 1 (a) and that prepared in Run 5 of Table 1 (b).

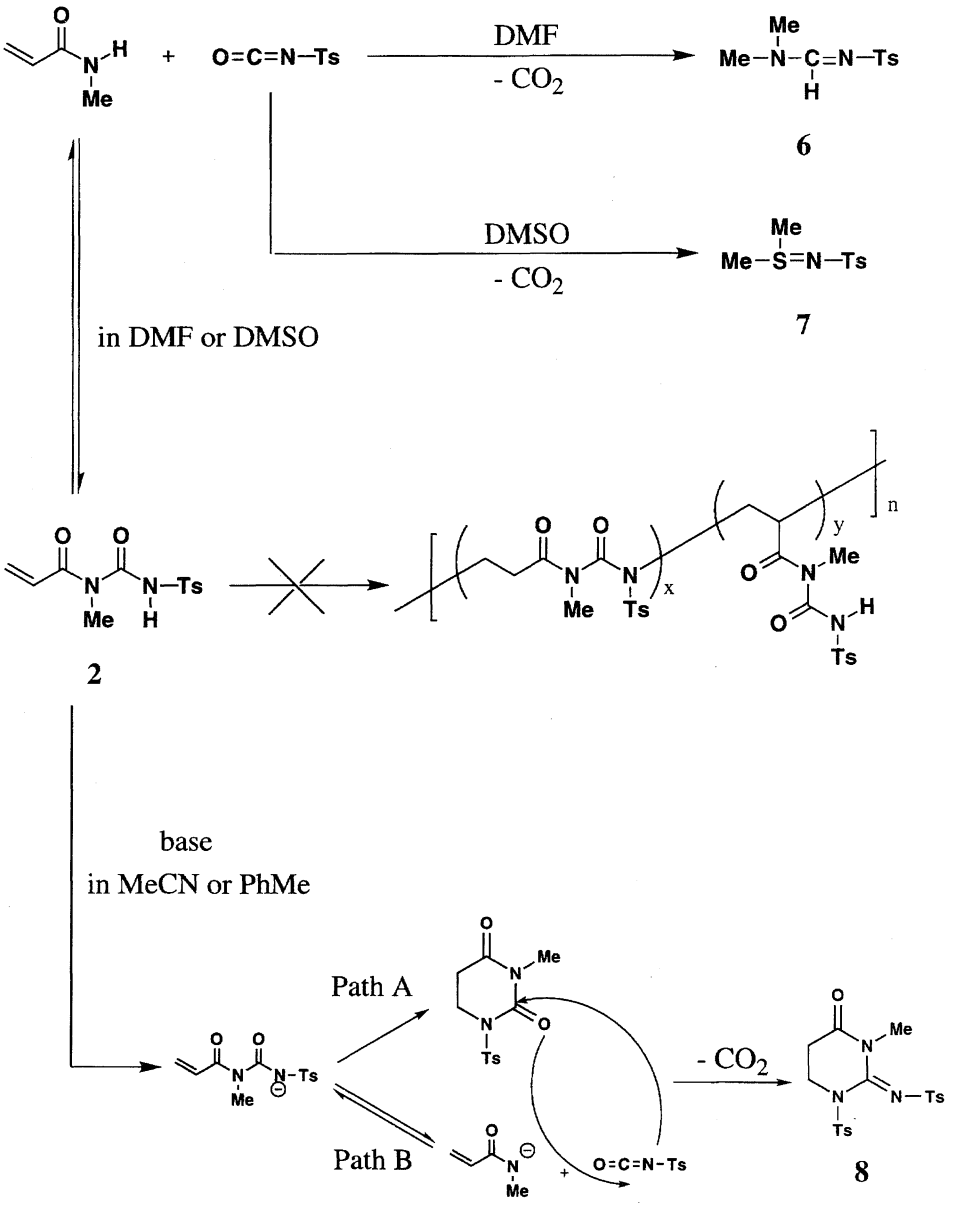
of these *N*-anions toward **1**. The lower yield of the polymers isolated by precipitation with diethyl ether, in comparison with the high monomer conversion, may be explained by considering that the present polymerization undergoes via the frequent hydrogen-transfer process, which is regarded as the chain-transfer reaction. In fact, basides the cyclic product(s), oligomeric products were detected in the diethyl ether-soluble fraction.

As mentioned above, the selectivity between the hydrogen-transfer and the vinyl polymerization was affected by the solvent and the concentration of the initiator. In the presence of an excess amount of *t*-BuOK, more than one proton might be abstracted from **1** and the resulting di- (or tri-) anions attack another monomer or its deprotonated form. In this case, the vinyl polymerization process might proceed predominantly, because the nucleophilicity of the carbanion should be higher that that of the *N*-anions. This might be the reason for the higher vinyl polymerization content of the

polymer produced in the presence of excess *t*-BuOK. When the polymerization was carried out in less polar solvents such as toluene, **1** did not dissolve enough in the solvents, due to which the relative concentration of *t*-BuOK to the dissolved monomer becomes higher. Consequently, the same mechanism might work also in less polar solvents, although 3 mol% of the initiator was employed.

When DBU (3 mol%) was used as an initiator for the polymerization of **1**, the high conversion of monomer **1** was observed irrespective of the solvents. By precipitation with diethyl ether, polymer **4** ($\overline{M}_n$ = 3700—4300) was obtained in 25—36% yield. From the structural elucidation of polymer **4** by ^{1}H NMR spectra, the obtained polymers were composed of both the hydrogen-transfer and the vinyl polymerization units whose ratio was not effected significantly by the solvents used for the polymerization.[19] Compared to the cases of *t*-BuOK, the counter cation (the protonated form of DBU) may be less interactive toward the propagating anion regardless of the solvent. By this process, the nucleophilicity of the carbanion (ii) might become strong enough to induce the vinyl polymerization.

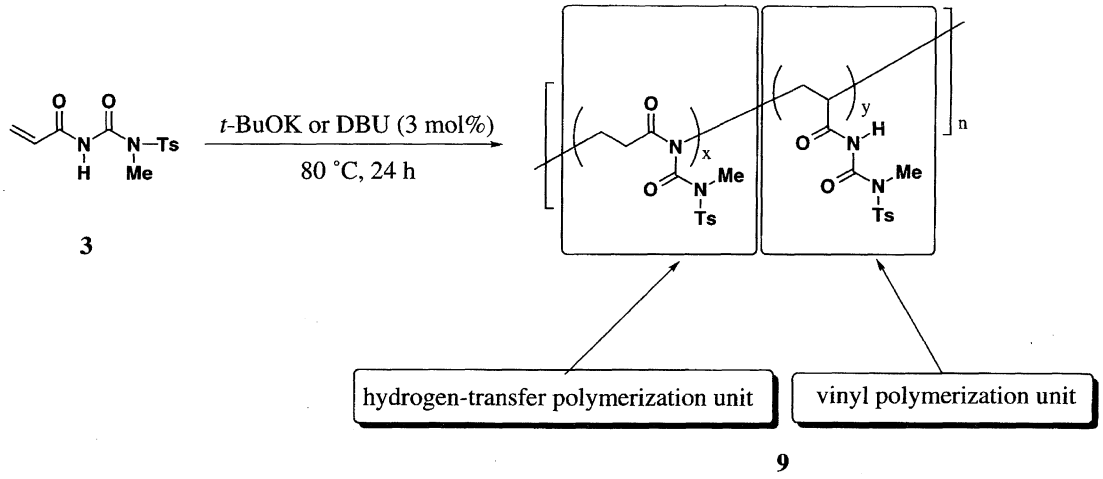
Hydrogen-Transfer Polymerization of 2 and 3. The monomers (**2** and **3**), in which either one of the two active hydrogens of **1** was masked with a methyl group, were subjected to the polymerization under the same conditions. In the case of *N*-acryloyl-*N*-methyl-*N'*-*p*-tolylsulfonylurea (**2**), the polymer was not produced and low molecular-weight products were obtained from the diethyl ether-insoluble part. The detailed analyses of the products showed that their structures were dependent upon the solvents used for the reaction. In DMF, a single product was obtained in 44 or 42% yield (by using *t*-BuOK or DBU, respectively) as a diethyl ether-insol-



Scheme 4.

uble part which was identified as *N,N*-dimethyl-*N'*-*p*-tolylsulfonylformamidine (**6**) by comparing the melting point and the FAB/MS spectrum with those of the authentic sample.[20] In DMSO, a compound identified as *S,S*-dimethyl-*N*-*p*-tolylsulfonylsulfimine (**7**)[20] was obtained in 55 or 59% yield (by using *t*-BuOK or DBU, respectively). In MeCN or toluene, a product (36—57% yield) was supported to be a cyclic product (**8**) by the FAB/MS spectra (*m/z* 436 $[M+H]^+$) as well as ^1H and ^{13}C NMR spectra.[21] The formation of these products (**6**—**8**) might be explained by assuming the decomposition of **2** into *p*-tolylsulfonyl isocyanate and *N*-methylacrylamide (Scheme 4). It is known that sulfonyl isocyanates react easily with amides and sulfoxides via the elimination of CO_2.[20] Thus, the products (**6** and **7**) obtained in DMF and DMSO might be regarded as the adducts of the isocyanate with the solvents. When the reaction was carried out in less nucleophilic solvents such as toluene or MeCN, the product (**8**) might be produced by the base-catalyzed intramolecular conjugate addition of **2**, and the subsequent condensation with the isocyanate. The decomposition of **2** rather than the polymerization might be due to the unstable character of **2** in comparison with **1**. That is, **2** does not have the imidic proton on the nitrogen atom, by which the stabilization by the enol form might be less than the case of **1**.

The hydrogen-transfer polymerization of *N*-acryloyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea (**3**) was also carried out under the same conditions. In this case, polymer **9** was obtained as a diethyl ether-insoluble product in moderate yield (Scheme 5 and Table 2). In contrast to **1**, monomer **3** could be dissolved in all the solvents used and the polymer produced by *t*-BuOK constantly had the specific hydrogen-transfer units which were independent of the solvents (Runs 1—4). In



Scheme 5.

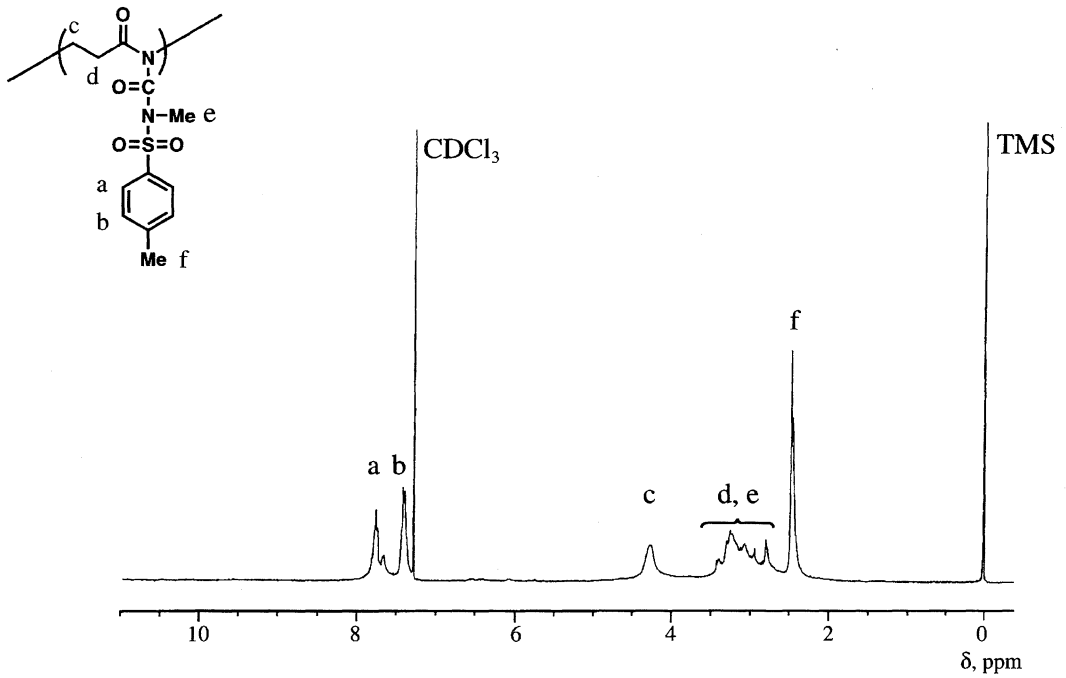


Fig. 2. ^1H NMR spectrum ($CDCl_3/CF_3COOH$) of **9** (Run 3, Table 2).

Fig. 2, the ^{1}H NMR spectrum of the polymer obtained in Run 3 is shown as a typical example. No methylene protons attributable to the vinyl polymerized structure were observed at $\delta = 1.00$—2.74, while those adjacent to the nitrogen were observed at $\delta = 3.60$—4.50 as a result of the hydrogen-transfer process. By using DBU (3 mol%), the polymerization proceeded both by the hydrogen-transfer and the vinyl polymerizations, whose ratio was determined as $x : y = 55 : 45$—67 : 33. Similar to the case of monomer **1**, the peak area of the aromatic protons observed in the ^{1}H NMR spectrum of polymer **9** was smaller than those expected from the peak intensities of the protons of the main chain (Table 2: Runs 1—4, by 0—10%; Runs 5—8, by 39—71%).[17] In this case, the eliminated *N*-methyl-*p*-toluenesulfonamide[22] was isolated from the diethyl ether-soluble part (43% yield in Run 5), which may indicate that side reactions accompanying the elimination of *N*-methyl-*p*-toluenesulfonamide from the side chain of the vinyl polymerization unit of polymer **9** takes place under the polymerization conditions.

Summary

The anionic polymerization behavior of monomers (**1**—**3**) derived from *p*-tolylsulfonyl isocyanate and acrylamide was examined in detail under various conditions. Although **2** decomposed to give rise low molecular-weight products presumably via the generation of the *p*-tolylsulfonyl isocyanate, monomers (**1** and **3**) were found to undergo the polymerization accompanying the hydrogen-transfer process. The selectivity between the hydrogen-transfer and the vinyl polymerization was affected by the initiators and by the solvents used for the polymerization.

References

1) O. C. Billeter, *Ber. Dtsch. Chem. Ges.*, **36**, 690 (1904); **37**, 2013 (1905).

2) W. Logemann, D. Artini, G. Tosolini, and F. Piccini, *Ber. Dtsch. Chem. Ges.*, **90**, 2527 (1957); **91**, 951 and 2566 (1958).

3) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).

4) T. Endo, M. Kanamaru, and T. Takata, *Macromolecules*, **27**, 3694 (1994).

5) M. Kanamaru, T. Takata, and T. Endo, *Macromolecules*, **27**, 7492 (1994).

6) M. Kanamaru, T. Takata, and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 1361 (1995).

7) M. Kanamaru, T. Takata, and T. Endo, *Macromolecules*, **28**, 7979 (1995).

8) M. Kanamaru, T. Takata, and T. Endo, *Macromol. Chem. Phys.*, **197**, 1795 (1996).

9) T. Iwamura, I. Tomita, M. Suzuki, and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, in press.

10) D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Am. Chem. Soc.*, **79**, 3760 (1957).

11) S. Okamura, Y. Oishi, T. Higashimura, and T. Senoo, *Koubunshi Kagaku*, **19**, 323 (1962).

12) H. Wexler, *Makromol. Chem.*, **115**, 262 (1968).

13) T. Tsunetsugu, T. Matsuo, and J. Furukawa, *Makromol. Chem.*, **107**, 222 (1967).

14) M. Guita, G. Camino, and L. Trossarelli, *Makromol. Chem.*, **131**, 309 (1970).

15) T. Iwamura, I. Tomita, M. Suzuki, and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, in press.

16) *N*-Propionyl-*N'*-methyl-*N'*-*p*-tolylsulfonylurea; ^{1}H NMR ($CDCl_3$, 90 MHz) $\delta = 1.16$ (t, $J = 7.29$ Hz, 3H, CH_3CH_2–), 2.47 (s, 3H, $CH_3C_6H_4$–), 2.71 (q, 7.29 Hz, 2H, CH_3CH_2–), 3.15 (s, 3H, –N–CH_3), 7.31 (d, $J = 8.37$ Hz, 2H, –C_6H_4–), 7.93 (d, $J = 8.37$ Hz, 2H, –C_6H_4–), 12.21 (bs, 1H, –CONH–). *N*-propionyl-*N*-*n*-butyl-*N'*-*p*-tolylsulfonylurea; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 0.85$—0.95 (m, 3H, CH_3CH_2–), 1.10—1.20 (m, 3H, CH_3CH_2–), 1.20—1.40 (m, 2H, $CH_3CH_2CH_2CH_2$–), 1.40—1.60 (m, 2H, $CH_3CH_2CH_2CH_2$–), 2.40—2.47 (m, 3H, $CH_3C_6H_4$–), 2.52—2.63 (m, 2H, –CO–CH_2–), 3.55—3.65 (m, 2H, –N–CH_2–), 7.38 (d, $J = 8.64$ Hz, 2H, –C_6H_4–), 7.74 (d, $J = 8.64$ Hz, 2H, –C_6H_4–), 9.96 (bs, 1H, –CONHSO$_2$–).

17) In the elemental analysis, the C and S contents of polymers were smaller than expected.

18) **5**; Yield 30%; IR (KBr) 3200 (NH), 1716 (C=O), 1381 (–SO_2–), 1186 (–SO_2–), 547 cm^{-1} (N–C=O); ^{1}H NMR (DMSO-d_6, 90 MHz) $\delta = 2.41$ (s, 3H, CH_3–C_6H_4–), 2.75 (t, $J = 6.50$ Hz, 2H, –CH_2–CH_2–CO–), 4.03 (t, $J = 6.50$ Hz, 2H, –N–CH_2–CH_2–), 7.43 (d, $J = 8.28$ Hz, 2H, C_6H_4), 7.87 (d, $J = 8.28$ Hz, 2H, C_6H_4), 10.79 (s, 1H, –CONHCO–); ^{13}C NMR (DMSO-d_6, 22.4 MHz) $\delta = 21.0$, 40.8, 128.0, 129.5, 135.4, 144.7, 149.7, 170.1; FAB/MS *m/z* 269 $[M+H]^+$.

19) Similar to the case of *t*-BuOK, the peak area of the aromatic protons were smaller than expected (Table 1: Runs 6—9, by 35—57%).

20) C. King, *J. Org. Chem.*, **25**, 352 (1960).

21) **8**; $R_f = 0.9$ (chloroform/methanol 9/1 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.45$ (s, 3H, CH_3–C_6H_4–), 2.47 (s, 3H, CH_3–C_6H_4–), 3.12 (s, 3H, CH_3–N–), 3.57 (t, $J = 6.40$ Hz, 2H, –CH_2–CH_2–CO–), 4.12 (t, $J = 6.40$ Hz, 2H, –N–CH_2–CH_2–), 7.36 (d, $J = 8.40$ Hz, 2H, –C_6H_4–), 7.39 (d, $J = 8.40$ Hz, 2H, –C_6H_4–), 7.80 (d, $J = 8.40$ Hz, 2H, –C_6H_4–), 7.89 (d, $J = 8.40$ Hz, 2H, –C_6H_4–); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 21.5$, 21.6, 28.6, 30.5, 39.3 126.6, 128.7, 129.5, 129.6, 134.8, 138.5, 143.6, 145.6, 149.4, 164.2; FAB/MS *m/z* 436 $[M+H]^+$. In the ^{13}C NMR spectrum of **8**, a signal due to a carbonyl group was observed at $\delta = 149.4$ which is close to the chemical shift of the signal due to the carbonyl group of the *N*-methyl amide moieties ($\delta = 150.1$) rather than that of the urea group ($\delta = 170.0$) in **3**. Thus, product **8** may have a structure as illustrated in Scheme 5.

22) *N*-Methyl-*p*-toluenesulfonamide; IR (KBr) 3275 (NH), 2984 (CH_3), 2928 (CH_3), 1319 (–SO_2–), 1157 (–SO_2–), 551 cm^{-1} (N–C=O); ^{1}H NMR ($CDCl_3$, 90 MHz) $\delta = 2.43$ (s, 3H, CH_3–C_6H_4–), 2.63 (d, $J = 2.70$ Hz, 3H, –N–CH_3–), 4.83 (bs, 1H, –NH–), 7.31 (d, $J = 8.19$ Hz, 2H, C_6H_4), 7.76 (d, $J = 8.19$ Hz, 2H, C_6H_4); ^{13}C NMR ($CDCl_3$, 22.4 MHz) $\delta = 21.4$, 29.2, 127.2, 129.7, 135.7, 143.4; FAB/MS *m/z* 186 $[M+H]^+$.