Cyclopolymerization of *N,N'*-Bis(phenylsulfonyl)-*N,N'*-divinylethylenediamine and the Related Monomer

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ABSTRACT: The cationic polymerization of 1,7-diene monomers **1a** and **1b** produced polymers **2a** and **2b** with seven-membered rings as a precursor of azacrown polymer. SnCl_4 and $\text{BF}_3 \cdot \text{OEt}_2$ in dichloromethane were effective for polymerization. Sulfuric acid was less effective and trifluoroacetic acid was ineffective. The molecular weights reached a maximum of 17000 and 34000 for **2a** and **2b**, respectively. Monomer **1a** polymerized with 100% cyclization. Although all the vinyl groups participated also in the polymerization of **1b**, GPC traces of **2b** showed a pronounced leading in the region of higher molecular weight by some participation of chain branching. The monomers were unstable to convert to 2-methylimidazolidines **9a** and **9b**, when allowed to stand in contact with the atmosphere. The polymerization formed seven-membered ring units, but the cyclization reaction resulted in five-membered ring compounds.

KEY WORDS *N,N'*-Divinyl Monomer / 1,7-Diene / Cyclopolymerization / Azacrown Polymer / Cationic Polymerization / Cyclization Reaction / Iminium Ion /

Cyclopolymerization is a direct and facile method of synthesizing polymers with crown-like units such as crown ethers, crown lactones and thiacrowns.¹ Macrocycles containing a nitrogen donor, namely, azacrowns complex more strongly with the transition and post-transition metal ions and capture strongly a fixed number of protons in the ring, which are entirely different from the characteristics of crown ethers.² Until recently, however, little attention was given to the syntheses of polymers with azacrown units *via* cyclopolymerization. Divinyl ethers,³ diacrylate and dimethacrylate⁴ derived from diaza-12-crown-4 yielded polymers with macrocycles containing mixtures of oxygen and nitrogen donor atoms. The greatest ability for complexing with Li^+ ion is a characteristic of the polymers. The *N*-vinyl group should be a key functional group for synthesizing the azacrown polymers by cyclopolymerization. *N*-Vinyl-*N*-methyl-*p*-toluenesulfonamide has been reported to polymerize not using radical initiators, but using cationic initiators.⁵ A synthetic route of the azacrowns includes the protection and regeneration of amino groups through *p*-toluenesulfonamides. The *N*-vinyl derivative of *p*-toluenesulfonamide, therefore, is well suited for the monomer design to obtain the azacrown polymers.

This article describes the cationic cyclopolymerization of *N,N'*-bis(phenylsulfonyl)- and *N,N'*-bis(*p*-tolylsulfonyl)-*N,N'*-divinylethylenediamines to obtain polymers with seven-membered ring units and the cyclization reaction of these monomers to yield 2-methylimidazolidines with five-membered rings.

EXPERIMENTAL

Materials

Dichloromethane and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride. Toluene was purified by the usual method and distilled from sodium-benzophenone. Borontrifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) and tin(IV) chloride (SnCl_4) were purified by the distillation of commercial products under reduced pressure and used as a solution in dry dichloromethane.

N,N'-Bis(phenylsulfonyl)-*N,N'*-bis(2-hydroxyethyl)ethylenediamine

The synthesis is similar to that used by Atkins *et al.* for the preparation of 3,6,9-tris(*p*-tolylsulfonyl)-3,6,9-triazaundecane-1,11-diol.⁶ From *N,N'*-bis(phenylsulfonyl)ethylenediamine (20.4 g, 60 mmol), ethylenecarbonate (11.6 g, 132 mmol), and potassium hydroxide (0.1 g), a colorless product was obtained (13.5 g, 53%). mp 133°C; ^1H NMR (270 MHz, CDCl_3): δ 7.85–7.50 (m, 10H, ArH), 3.91 (t, $J=4.3$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.49 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), and 3.28 ppm (t, $J=4.3$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{N}$); ^{13}C NMR (68 MHz, CDCl_3): δ 137.98, 132.99, 129.30, and 127.32 (ArC), 61.11 (OCH_2), and 53.12 and 50.33 ppm (NCH_2). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_6\text{S}_2$: C, 50.45%; H, 5.64%; N, 6.54%; S, 14.97%. Found: C, 50.36%; H, 5.47%; N, 6.48%; S, 14.97%.

3,6-Bis(phenylsulfonyl)-3,6-diazaoctane-1,8-di(*p*-toluenesulfonate)

The synthesis is similar to that used by Szeja for the preparation of sulfonic esters under phase-transfer catalyzed conditions.⁷ From *N,N'*-bis(phenylsulfonyl)-

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N,N'-bis(2-hydroxyethyl)ethylenediamine (21.9 g, 51 mmol), tosyl chloride (23.5 g, 123 mmol), and benzyltriethylammonium chloride (0.6 g), a colorless product was obtained (27.7 g, 76%). mp 134°C; ^1H NMR (270 MHz, CDCl_3): δ 7.86–7.32 (m, 18H, ArH), 4.14 (t, $J=5.3$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.39 (t, $J=5.3$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.33 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), and 2.43 ppm (s, 6H, CH_3); ^{13}C NMR (68 MHz, CDCl_3): δ 145.16, 137.94, 133.05, 132.27, 129.99, 127.95, and 127.29 (ArC), 68.83 (OCH_2), and 49.70 and 49.39 ppm (NCH_2), and 21.60 (CH_3). *Anal.* Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_2\text{O}_{10}\text{S}_4$: C, 52.16%; H, 4.92%; N, 3.80%; S, 17.40%. Found: C, 52.05%; H, 4.95%; N, 3.83%; S, 17.62%.

N,N'-Bis(phenylsulfonyl)-*N,N'*-divinylethylenediamine (**1a**)

A solution of 3,6-bis(phenylsulfonyl)-3,6-diazoctane-1,8-di(*p*-toluenesulfonate) (7.37 g, 10 mmol) in dry DMF (45 ml) was added to a suspension of sodium hydride (1.6 g) in dry DMF (25 ml) during 2 h at 50°C. The reaction mixture was stirred overnight at room temperature and diluted with ice-water. The precipitate was filtered off, washed four times with water (50 ml portions) and then with ethanol (50 ml) and dried. The crude product was purified by column chromatography on aluminum oxide with chloroform and by recrystallization from dichloromethane/ethanol to give pure **1a** as a white powder (2.1 g, 54%). mp 169–170°C; ^1H NMR (270 MHz, CDCl_3): δ 7.80–7.26 (m, 10H, ArH), 6.89 (dd, $J=15.8$ and 9.2 Hz, 2H, $\text{CH}_2=\text{CH}$), 4.61 (dd, $J=15.8$ and 2.0 Hz, 2H, $\text{CH}_2=\text{CH}$), 4.43 (dd, $J=9.2$ and 2.0 Hz, 2H, $\text{CH}_2=\text{CH}$), and 3.55 ppm (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$); ^{13}C NMR (68 MHz, CDCl_3): δ 138.68, 133.39, 129.54, and 126.98 (ArC), 131.75 ($\text{CH}_2=\text{CH}$), 93.19 ($\text{CH}_2=\text{CH}$), and 41.54 ppm ($\text{NCH}_2\text{CH}_2\text{N}$). *Anal.* Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$: C, 55.08%; H, 5.14%; N, 7.14%; S, 16.34%. Found: C, 54.95%; H, 4.96%; N, 6.99%; S, 16.26%.

N,N'-Bis(*p*-tolylsulfonyl)-*N,N'*-divinylethylenediamine (**1b**)

The synthesis is similar to that used for **1a**. mp 182–183°C; ^1H NMR (270 MHz, CDCl_3): δ 7.64 (d, $J=8.1$ Hz, 4H, ArH), 7.31 (d, $J=8.1$ Hz, 4H, ArH), 6.88 (dd, $J=15.7$ and 9.2 Hz, 2H, $\text{CH}_2=\text{CH}$), 4.59 (dd, $J=15.7$ and 1.6 Hz, 2H, $\text{CH}_2=\text{CH}$), 4.40 (dd, $J=9.2$ and 1.6 Hz, 2H, $\text{CH}_2=\text{CH}$), 3.51 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), and 2.42 ppm (s, 6H, ArCH₃); ^{13}C NMR (68 MHz, CDCl_3): δ 144.15, 135.53, 129.95, and 126.86 (ArC), 131.66 ($\text{CH}_2=\text{CH}$), 92.70 ($\text{CH}_2=\text{CH}$), 41.48 ($\text{NCH}_2\text{CH}_2\text{N}$), and 21.53 ppm (ArCH₃). *Anal.* Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$: C, 57.12%; H, 5.75%; N, 6.66%; S, 15.25%. Found: C, 56.92%; H, 5.77%; N, 6.73%; S, 15.08%.

N,N'-Bis(phenylsulfonyl)-2,3-dimethylpiperazine (a mixture of (2*RS*,3*RS*)- and (2*RS*,3*SR*)-forms) (**3**)

Model compound **3** was prepared from *N,N'*-bis(phenylsulfonyl)ethylenediamine-*N,N'*-disodium salt and 1,2-dimethylethylene di(*p*-toluenesulfonate). mp 137–137.5°C; IR (KBr): 1446, 1342, 1166, 1085, 987, 732, 692, 620, and 590 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3): δ 7.77–7.73 (m, 4H, ArH), 7.60–7.48 (m, 6H, ArH), 3.91 (q, $J=6.7$ Hz, 2H, CH), 3.67 (m, 2H, CH_2),

3.08 (m, 2H, CH_2), and 0.98 ppm (d, $J=6.7$ Hz, 6H, CH_3) for (2*RS*,3*RS*)-form, and 3.65 (m, 2H, CH_2), 3.41 (q, 2H, CH), 3.23 (m, 2H, CH_2), and 0.93 ppm (d, 6H, CH_3) for (2*RS*,3*SR*)-form; ^{13}C NMR (68 MHz, CDCl_3): δ 140.21, 132.69, 129.23, and 126.83 (ArC), 53.67 (CH), 39.33 (CH_2) and 14.19 ppm (CH_3) for (2*RS*,3*RS*)-form, and 56.51 (CH), 44.56 (CH_2) and 13.77 ppm (CH_3) for (2*RS*,3*SR*)-form. *Anal.* Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$: C, 54.80%; H, 5.62%; N, 7.10%; S, 16.26%. Found: C, 54.74%; H, 5.59%; N, 6.93%; S, 16.36%.

N,N'-Bis(phenylsulfonyl)-1,5-diaza-2,4-dimethylcycloheptane ((2*RS*,4*RS*)-form) (**4**)

Model compound **4** was prepared from *N,N'*-bis(phenylsulfonyl)ethylenediamine-*N,N'*-disodium salt and 1,3-dimethyltrimethylene di(*p*-toluenesulfonate). mp 138–139°C; IR (KBr): 1446, 1336, 1321, 1153, 1087, 995, 732, 691, 621, and 570 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3): δ 7.81–7.78 (m, 4H, ArH), 7.57–7.47 (m, 6H, ArH), 4.00 (m, 2H, CH), 3.59 (s, 4H, NCH_2), 2.12 (m, 1H, CCH_2C), 1.97 (m, 1H, CCH_2C), and 1.21 ppm (d, $J=7.1$ Hz, 6H, CH_3); ^{13}C NMR (68 MHz, CDCl_3): δ 141.99, 132.31, 129.05, and 126.49 (ArC), 53.54 (CH), 48.15 (NCH_2), 43.67 (CCH_2C) and 19.75 ppm (CH_3). *Anal.* Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$: C, 55.86%; H, 5.92%; N, 6.86%; S, 15.70%. Found: C, 56.10%; H, 5.85%; N, 6.72%; S, 15.62%.

N,N'-Bis(phenylsulfonyl)-2-methylimidazolidine (**9a**)

mp 165–166°C; ^1H NMR (270 MHz, CDCl_3): δ 7.75–7.27 (m, 10H, ArH), 5.26 (q, $J=5.9$ Hz, 1H, CH), 3.43 (m, 2H, CH_2), 3.19 (m, 2H, CH_2), and 1.58 ppm (d, $J=5.9$ Hz, 3H, CH_3); ^{13}C NMR (68 MHz, CDCl_3): δ 137.30, 133.21, 129.30, and 127.41 (ArC), 71.64 (CH), 45.84 (CH_2), and 23.99 ppm (CH_3). *Anal.* Calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4\text{S}_2$: C, 52.44%; H, 4.95%; N, 7.64%; S, 17.50%. Found: C, 52.71%; H, 4.88%; N, 7.40%; S, 17.45%.

N,N'-Bis(*p*-tolylsulfonyl)-2-methylimidazolidine (**9b**)

mp 156–157°C; ^1H NMR (270 MHz, CDCl_3): δ 7.53 (d, $J=8.1$ Hz, 4H, ArH), 7.20 (d, $J=8.1$ Hz, 4H, ArH), 5.14 (q, $J=5.9$ Hz, 1H, CH), 3.42 (m, 2H, CH_2), 3.11 (m, 2H, CH_2), 2.42 (s, 6H, CH_3), and 1.58 ppm (d, $J=5.9$ Hz, 3H, CH_3); ^{13}C NMR (68 MHz, CDCl_3): δ 143.87, 134.06, 129.68, and 127.50 (ArC), 71.48 (CH), 45.74 (CH_2), 24.03 (CH_3), and 21.44 ppm (ArCH₃). *Anal.* Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$: C, 54.80%; H, 5.62%; N, 7.10%; S, 16.26%. Found: C, 54.97%; H, 5.53%; N, 7.13%; S, 16.20%.

Typical Polymerization Procedure

Monomer **1a** (314 mg, 0.8 mmol) was dissolved in dry dichloromethane (8.0 ml), and then a solution of SnCl_4 in dichloromethane (1.18 mol l^{-1} ; 34.0 μl , 0.04 mmol) was added at 0°C using a microsyringe. After 20 min, the solution was poured into a large amount of methanol containing a drop of aqueous ammonia, and the polymer obtained was purified by reprecipitation from dichloromethane/methanol and dried in a vacuum (295 mg, 94%). IR (KBr): 1446, 1332, 1311, 1155, 1089, 732, 690, and 582 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3): δ 8.60–6.74 (br, 10H, ArH), 5.17–2.45 (br), and 2.45–0.25 (br);

^{13}C NMR (68 MHz, CDCl_3): 140.71, 132.97, 129.94, and 127.10 (ArC), 50.97, 45.78, and 37.01 ppm. *Anal.* Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$: C, 55.08%; H, 5.14%; N, 7.14%; S, 16.34%. Found: C, 54.95%; H, 5.20%; N, 6.97%; S, 16.23%.

RESULTS AND DISCUSSION

Cyclopolymerization

Monomers **1a** and **1b** underwent polymerization with cationic initiators, though they exhibited no polymerization tendency toward radical initiators. The results of the cationic polymerization are listed in Table I. SnCl_4 and $\text{BF}_3 \cdot \text{OEt}_2$ were effective for the polymerization. The reaction system was homogeneous up to high conversion in the dichloromethane solution. The monomers were sparingly soluble in nitroethane and toluene. As the polymerization proceeded, the monomers gradually dissolved into the polymerization system and the system became homogeneous. Below a monomer concentration of 0.036 mol l^{-1} and above 60°C , a clear solution was obtained in toluene. Sulfuric acid was less effective and trifluoroacetic acid was ineffective for the polymerization.

The obtained polymers were colorless powders, soluble in toluene, nitroethane, and dichloromethane. Polymer **2a** obtained using the SnCl_4 system has a molecular weight ranging from 2600 to 17000, and that obtained using the $\text{BF}_3 \cdot \text{OEt}_2$ system ranged from 3000 to 8200. The degree of polymerization (DP) reached a maximum of 43 and 21, respectively. Maximum molecular weights for polymer **2b** were 34000 and 13000 for SnCl_4 and $\text{BF}_3 \cdot \text{OEt}_2$ in dichloromethane, corresponding to a DP of 81 and 31. Polymers **2a** and **2b** showed a unimodal distribution in GPC analysis, but the latter showed a

pronounced leading in the region of higher molecular weights. The tolylsulfonyl group, which is more bulky than the phenylsulfonyl group, should disturb the intramolecular cyclization in the polymerization process, resulting in chain branching for polymer **2b**. Gel-free polymers at very high conversion, however, are suggestive of a low tendency for branching.

The ^1H NMR analysis showed that the characteristic signals due to the vinyl groups at 6.89, 4.61, and 4.43 ppm disappeared after polymerization for monomers **1a** and **1b**, and thus, **1a** polymerized with 100% cyclization. The polymerization proceeded according to a cyclopolymerization mechanism leading to the polymers consisting of cyclic constitutional repeating units. The copolymerization of monomer **1a** (M_1) with isobutyl vinyl ether (M_2) in a feed molar ratio of 1/1 yielded the copolymer with the M_1/M_2 of 0.73/0.27 at a 72% conversion. The copolymer showed a unimodal distribution in GPC analysis. The characteristic signals due to the vinyl groups also disappeared in the ^1H NMR spectrum of the copolymer. The intramolecular cyclization of monomer **1a** is little inhibited by incorporation of the comonomer, isobutyl vinyl ether, thus indicating that monomer **1a** has a great tendency for cyclopolymerization.

Polymer Structure

The cyclopolymerization of the monomers corresponding to a 1,7-diene has a possibility of forming polymers with six-, seven-, and eight-membered rings. The intramolecular cyclization and the intermolecular reaction through tail-to-tail and head-to-head additions, respectively, form the constitutional units with eight-membered rings, whereas the duplicate head-to-tail additions lead to the formation of seven-membered rings, and the head-to-head and tail-to-tail additions to that of six-membered rings. The steric crowd of the arylsulfonyl groups in the polymer chain prevents the possibility of forming eight-membered rings. Therefore, *N,N'*-bis(phenylsulfonyl)-2,3-dimethylpiperazine (**3**) and *N,N'*-bis(phenylsulfonyl)-1,5-diaza-2,4-dimethylcycloheptane (**4**) were synthesized as model compounds for the six- and seven-membered constitutional units, respectively. In the

Table I. Cationic polymerizations of *N,N'*-bis(phenylsulfonyl)- and *N,N'*-bis(*p*-tolylsulfonyl)-*N,N'*-divinylethylenediamine (**1a** and **1b**)^a

Monomer (M)	Catalyst (C)	Solvent	[M]	Temp	Time	Conv.	M_n^b	M_w/M_n
			mol l^{-1}	$^\circ\text{C}$	min	%	$\times 10^{-3}$	
1a	SnCl_4	$\text{C}_6\text{H}_5\text{CH}_3$	0.036	0	60	33	2.7	1.24
		CH_2Cl_2	0.1	0	20	94	17	2.24
		CH_2Cl_2	0.1	-78	20	15	2.6	1.55
	$\text{BF}_3 \cdot \text{OEt}_2$	$\text{C}_2\text{H}_5\text{NO}_2$	0.1	0	20	89	8.6	1.63
		$\text{C}_6\text{H}_5\text{CH}_3$	0.036	0	60	55	3.0	1.43
		CH_2Cl_2	0.1	0	20	90	8.2	1.84
		$\text{C}_2\text{H}_5\text{NO}_2$	0.1	0	20	90	7.6	1.58
		CH_2Cl_2	0.1	0	20	11	1.4	1.08
	H_2SO_4	CH_2Cl_2	0.2	0	20	72	7.4	1.59
	SnCl_4	CH_2Cl_2	0.1	0	20	89	34	— ^c
1a/IBVE 1b	SnCl_4	CH_2Cl_2	0.1	-78	20	13	3.6	2.43
		$\text{C}_2\text{H}_5\text{NO}_2$	0.1	0	20	87	8.9	3.10
		CH_2Cl_2	0.1	0	20	79	13	— ^c
	$\text{BF}_3 \cdot \text{OEt}_2$	CH_2Cl_2	0.1	0	20	76	5.4	3.80
		$\text{C}_2\text{H}_5\text{NO}_2$	0.1	0	20	0	—	—
	$\text{CF}_3\text{CO}_2\text{H}$	CH_2Cl_2	0.1	0	20	0	—	—

^a $[\text{M}]/[\text{C}] = 20$. ^b Determined by GPC using polystyrene as standard. ^c GPC traces showed a pronounced leading in the region of higher molecular weight.

IR spectra of polymer **2a** and model compounds **3** and **4**, the characteristic bands for ν SO (asym), ν SO (sym), and ν C–N appeared at 1332 and 1311, 1155, and 1089 cm^{-1} , for **2a**, at 1342, 1166, and 1085 cm^{-1} for **3**, and at 1336 and 1321, 1153, and 1087 cm^{-1} for **4**. The IR spectral characteristics of polymer **2a** are in good agreement with those of **4**. In the ^1H NMR spectrum of polymer **2a**, the broad signals in the range 0.5–5.0 ppm gave no marks of identification. The ^{13}C NMR spectrum of polymer **2a** showed three characteristic signals due to the methylene and methine carbons at 37.01, 45.78, and 50.97 ppm. The signal at 50.97 ppm is due to the methine carbon corresponding to that for **4**. Because of broadening, the signal at 45.78 may be composed of two distinct carbons corresponding to two kinds of methylene carbons for **4**. The signal at 37.01 ppm may be assigned to the methylene carbon in the main chain. The ^{13}C NMR spectral characteristics of polymer **2a** are compatible with those of **4** rather than those of **3**. A small signal is found in the vicinity of 39 ppm barely for polymer **2a**, but clearly for polymer **2b**. Its assignment, however, is obscure.

Most of the cationic vinyl polymerizations are highly regioselective due to the much greater stability of tertiary and secondary carbenium ions compared to primary carbenium ions. In cationic polymerization, ethylene glycol divinyl ether being a 1,7-diene produced the polymer with seven-membered rings.⁸ The nitrogen donor atom causes an increase in the reactivity of *N*-vinyl groups not only through the inductive effect, but also through the resonance effect. In addition, the stability of the carbocation derived from the *N*-vinyl group is given a profound contribution from resonance structures **5A** and **5B** for iminium ion. The polymerization process of monomers **1a** and **1b**, thus, should be preferable to induce head-to-tail additions, resulting in the formation of seven-membered rings.

Cyclization Reaction to 2-Methylimidazolidines

Monomers **1a** and **b** were unstable when allowed to stand in contact with the atmosphere. The monomers purified by column chromatography were converted into a mixture of two components during several days. Figure 1 shows a change in the ^1H NMR spectrum of monomer **1b** on storage. The specimen in a normal NMR tube was closed with a Teflon plug. Characteristic proton resonances due to the vinyl groups were weakened with the appearance of new resonances at 9.78, 5.14, 3.42, 3.11, 2.20, and 1.58 ppm after 20 h and all the resonances due to monomer **1b** practically disappeared after 4 days.

Figure 1. Variation in ^1H NMR spectra of *N,N'*-bis(*p*-tolylsulfonyl)-*N,N'*-divinylethylenediamine (**1b**): a) immediately after the measurement, b) after 20 h, c) after 4 days in a normal NMR tube with a Teflon plug, and d) after 4 days in a sealed tube.

The specimen in a sealed tube, however, did not undergo the conversion, thus resulting in a low yield even after 4 days, as shown in Figure 1d.

A reaction of monomer **1b** (0.42 g, 1 mmol) with trifluoroacetic acid (0.1 ml, 1.3 mmol) in chloroform (10 ml) for 4 h at room temperature afforded pale yellow crystals (0.41 g). On purification by column chromatography on silica gel with chloroform, a colorless crystal (0.16 g) was obtained. The resulting compound showed the ^1H NMR spectrum in which the signals coincided in chemical shift with those, except for the absorptions at 9.78 and 2.20 ppm, in the spectrum of the specimen observed after 4 days.

The ^1H , ^{13}C , and ^1H – ^{13}C 2D NMR analyses established that the obtained compound is *N,N'*-bis(*p*-tolylsulfonyl)-2-methylimidazolidine (**9b**). On the other hand, the compound having the characteristic signals at 9.78 (quartet) and 2.20 (doublet) ppm should be acetaldehyde. The experience of preparing 2,4-dinitrophenylhydrazone confirmed the formation of acetaldehyde during the reaction of **1b** with trifluoroacetic acid. Therefore, the storage led to the conversion of monomer **1b** into **9b** and acetaldehyde. The conversion was observed also in monomer **1a**. Consequently, the dissolved water in the solvent and further moisture in the air promoted the conversion of **1** to **9**.

The unassigned peaks at 5.77 (quartet) and 1.28 (doublet) ppm are still found in Figures 1b and 1d. Because of their disappearance after the completion of the reaction, the signals should be assigned to the intermediate species in the conversion of **1b** to **9b**. Both signals at 5.77 and 1.28 ppm have the *J* coupling value of 5.9 Hz, which equals that at 5.14 and 1.58 ppm for **9b**.

The ratio of the peak areas at 5.77 and 1.28 ppm is 1 : 3. The result suggests that the intermediate species is **6** or **7**. Because the proton signal of CH₃-C for the iminium salts is observed in the range of 2.5—2.8 ppm,⁹ the species is not assigned to **6**. The methyl and methine proton signals in CH₃CH(OH)N⁺R₁R₂R₃ are shifted to lower fields by the β- and α-effects, respectively, of the ammonium ion in comparison with the signals at 1.16 and 3.94 ppm in isopropanol. The intermediate species, therefore, is tentatively assigned to structure **7**.

Iminium salts are rapidly hydrolyzed with the formation of the carbonyl component and a secondary ammonium salt in contact with water.¹⁰ Therefore, monomers **1** are transformed into iminium ions **6** by capturing a proton. Moisture induces the rapid hydrolysis of **6** to ammonium ions **7**, and then the intramolecular proton transfer from the secondary ammonium ions to the *N*-vinyl groups brings about cyclization into five-membered rings **9**. Under dry atmosphere during polymerization, iminium ions **6** favor the process of forming polymers **2** through intramolecular cyclization.

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