8992 *Macromolecules* **2000,** *33,* 8992−9001

Covalent Cross-Linking of Polymers through Ionene Formation and Their Thermal De-Cross-Linking

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Received April 10, 2000; Revised Manuscript Received September 21, 2000

ABSTRACT: Quaternization and dequaternization of tertiary amines were employed to generate thermally reversible covalent ionene networks. Chlorine or tertiary amine containing polymers were cross-linked with ditertiary amines and dihalide compounds, respectively, to generate ionene networks. The cross-linking reactivity of the dihalide decreased with decreasing carbonium ion character of its alkyl, and the reactivity of the ditertiary amine was dependent on the steric effect of its alkyl groups and the flexibility of the alkyl connecting the two nitrogen atoms of its molecule. IR and NMR tests, reactive solubility experiments and conductivity, differential scanning calorimetry, and flowability (at 215 °C) determinations have been carried out to investigate the thermal reversibility of cross-linked polymers. The thermal de-cross-linking/re-cross-linking was markedly affected by the nature of the tertiary amine and halide that took part in quaternization. Poor reversibility was found when the Cl-containing polymer was cross-linked with a diamine whose nitrogen atoms belonged to a saturated ring, such as dipiperidinomethane and 1,4-dimethylpiperazine. The de-cross-linking and re-cross-linking were rapid when either one or both bridging alkyls of the nitrogen atoms possessed a higher carbonium ion character than the two nonbridging alkyls. The (co)polymers obtained through the (co)polymerization of chloromethylstyrene, 2-(dimethylamino)ethyl acrylate, or vinylpyridine could be effectively quaternized with selected cross-linkers under moderate conditions to generate networks that exhibited thermal reversibility.

Introduction

Ionenes are polymers that contain quaternary amines in their backbones and can be obtained through the Menschutkin reaction between a dihalide and a ditertiary amine. Numerous papers regarding the preparation, the properties, and the applications of linear ionenes have been reported since the systematic research conducted by Rembaum's group.[1] As well-known, the reversible Menschutkin reaction of a quaternary ammonium occurs at elevated temperatures.[2] In fact, the dequaternization of ionenes at temperatures around 200 °C was frequently regarded as a negative feature (decomposition) of ionene polymers.[3] However, very limited results were reported about the thermally reversible dequaternization at high temperatures and requaternization at low temperatures of ionenes. In the past 3 decades, a number of papers[3b−d,4] became available regarding the elastomeric ionene polymers that contained ionene segments and soft blocks in their backbone. These polymers were considered physically cross-linked elastomers because of ion pair interactions. There are also reports dealing with the cross-linking of polymers via ionene covalent bridges.[5] One of them was concerned with a rubber that contained about two ionene bridges per polymer chain and could de-cross-link under mechanical shear and re-cross-link under resting conditions, due to reversible dequaternization.[5d] While the possibility of a thermally reversible cross-linking via ionene bridges was mentioned by Engle and Wagener,[6] no experimental investigation was yet carried out. Only the thermally reversible chain extension of poly(tetramethylene oxide) (PTMO) was studied by Leir et al.[7]

Numerous attempts have been made in the past 3 decades to develop thermally reversible covalent (TRC) cross-linking of polymers, because such cross-linked polymers are expected to be similar to the thermosetting polymers as concerns their physical properties and solvent resistance and can be remolded by thermal processing technologies.[6,8] Several thermally reversible systems, reviewed in ref 6, have been proposed. It should be, however, emphasized that the reactions do not fully reverse; nevertheless, they reverse enough for the de-cross-linking to provide thermoplasticity to the cross-linked polymers.

In the present paper the quaternization/dequaternization of quaternary ammoniums was applied to polymer cross-linking through ionene covalent bridges. These experiments were attempted because (1) no catalyst and no third component are required for the quaternization/dequaternization equilibrium which is controlled only by temperature; (2) the polymer network can be generated at a high rate under moderate conditions, because of the facile formation of the ionene moieties; (3) the dequaternization temperatures of most ionenes are around 200 °C,[3,9] the temperature employed in the thermal processing of many traditional polymers; and (4) the electrostatic resistance of the cross-linked polymers can be improved by the ammonium salt ionic pairs, which provide a higher conductivity than the hydrocarbon chains.

For the above reasons, the cross-linking reactions between (1) Cl-containing polymers and bifunctional tertiary amines, (2) polymers containing pendant tertiary amino groups and dihalide compounds, and (3) Cl-containing polymers and polymers containing pendant tertiary amino groups were carried out (Scheme 1). The thermal reversibility of these cross-linked polymers was investigated through IR and NMR tests, reactive solubility, differential scanning calorimetry (DSC), and conductivity and flowability measurements on heating.

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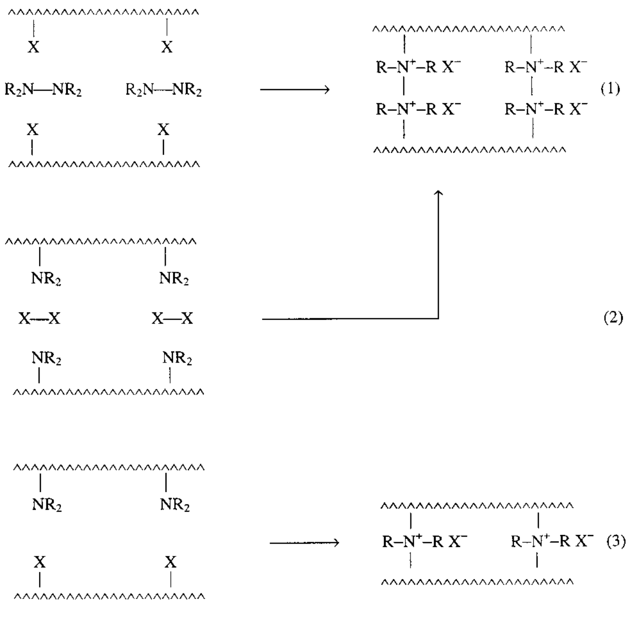
10.1021/ma0006272 CCC: $19.00

Scheme 1



Where X= halide; R= alkyl

Experimental Section

Materials. All materials were purchased from Aldrich except when noted otherwise. Styrene (St, 99%), butyl acrylate (BA, Fluka, >99%), chloromethylstyrene (CMS, 90%), and 2-(dimethylamino)ethyl acrylate (DMAEA, 98%) were distilled under reduced pressure before use. The solvents and the following chemicals were used as supplied: potassium persulfate (KPS, 99.99%), dodecyl sulfate sodium salt (98%), 4-*tert*-butylcatehol (TBC, 97%), 1,3-dichloroacetone (DCA, 95^+%), 1,4-dichlorobutane (DCB, 99%), 1,4-dibromobutane (DBB, 99%), α,α′-dichloro-*p*-xylene (DCX, 98%), α,α′-dibromo-*p*-xylene (DBX, 97%), benzyl bromide (BzB, 98%), benzyl chloride (BzC, Mallinckrodtt, Analytical Reagent, boiling range 177.1−179.3 °C), *N*,*N*-dimethylbenzylamine (DMBA, 99^+%), triethylamine (99%), *N*,*N*,*N*′,*N*′-tetramethyl-1,4-butanediamine (TMBDA, 98%), *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA, 99.5%), *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine (TMHDA, 99%), *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB, 97%), *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA, 98%), 2,2′-dipyridyl (DPD, 99^+%), 4,4′-trimethylenedipyridine (TMDPD, 98%), dipiperidinomethane (DPDM, 98%), 1,4-dimethylpiperazine (DMP, 98%). The following commercial polymers were used as received: poly(vinyl chloride) (PVC, inherent viscosity 0.51, $M_w = 71\,600$ by GPC), chlorinated polypropylene (CPP, 32 wt % chlorine, $M_w = 150\,000$), polyepichlorohydrin (PECH, $M_w = 700\,000$), poly(chloromethylstyrene) (PCMS, 60/40 mixture of 3- and 4-isomers, $M_w = 55\,000$), poly(4-vinylpyridine) (PVP, average $M_w = 60\,000$, T_g (onset, annealed) 137 °C).

Emulsion Polymerization. The polymerization was carried out under the conditions listed in Table 1. The polymer was separated from emulsion by adding methanol (containing 2 wt % TBC), then kept in water overnight, and washed twice with distilled water before being vacuum-dried at about 60 °C.

Cross-Linking Reaction. The reaction was carried out with magnetic stirring under a N_2 atmosphere by adding to a polymer solution the cross-linker and 0.1 wt % (based on the solvent) of TBC (as inhibitor to avoid the formation of free radicals during heating). The duration up to the moment at which the magnetic stirring stopped was considered as gelation time. The gel was cut into small pieces, and the solvent was extracted from the gel with methanol. The obtained polymer pieces were then submerged into distilled water for 12 h and washed three times with distilled water and twice with methanol before being vacuum-dried at about 60 °C.

Thermocompression of the Cross-Linked Polymer. A polymer specimen with a thickness of about 1.5−2 mm was first prepared from small pieces (of about 0.5 mm size) of cross-linked polymer, using a macro−micro KBr die. Then the obtained specimen was placed between two plates and pressed for about 10 min with a Carver Laboratory Press (model C) at about 215 °C under a pressure of about 700 psi. Subsequently, the polymer specimen was pressed again at room temperature (about 15 min) in another Carver Press under a pressure of about 1200 psi, to produce a polymer film with a thickness of about 0.2 mm. The obtained film was cut into small pieces which were piled up in four or five layers before being again subjected to compression. The two plates were coated with Silicone Fluid SF 96/50 (THOMAS SCIENTIFIC) to facilitate the release after compression.

Measurements. ^{1}H NMR spectra were recorded in $DCCl_3$ (99.8 atom % D, 0.05 vol % tetramethylsilicone) or in a mixture of $DCCl_3$ and THF-d_8 (99.5 atom % D) on a VXR-400 spectrometer. The cross-linked polymer was ground as a fine powder before being introduced into the NMR tube. The FT-IR spectra were recorded on a Perkin-Elmer 1760-X spectrometer. Gel permeation chromatography (GPC, Waters) measurements were carried out using THF as solvent, at 30 °C. The gel content of the cross-linked polymer (denoted gel %) was determined by wrapping 0.1 g of cross-linked polymer in a filter paper (Whatman, Φ90 mm) and subjecting it for 10 h to extraction with refluxed THF in a Soxhlet equipment. The package was then vacuum-dried at a temperature of about 60 °C, until a constant weight was reached. The gel % was calculated from the weight increase above that of the filter paper and the original weight of the polymer tested. The insoluble percentage of cross-linked polymer after its treatment with a monofunctional halide compound or tertiary amine (denoted gel′ %) was obtained as follows: 0.1 g of cross-linked polymer was introduced into 5 g of a solvent containing a monofunctional compound and 0.3 wt % (based on solvent) TBC and heated in an oil bath at various temperatures. The mixture was then filtered through a medium fast filter paper, well wrapped up with such paper, and subjected to the same extraction and drying procedures employed in the determination of the gel % described above. The following method was employed in the conductivity measurements. Two stainless steel plates (5 mm × 20 mm), each connected to one of the electrodes of a conductivity cell (cell constant, $K = 1.10$, at 25 °C), were placed parallel to each other at a distance δ of 0.3 cm into a small test tube (volume ca. 2 mL). A mixture of a polymer solution and a cross-linker was then added to the test tube that was plugged with a rubber stopper and further sealed by winding with a Teflon tape. The conductivity cell was connected to a Jenway 4010 conductivity meter to detect the conductivity during gelation and during heating (at a rate of about 8 °C/min) and cooling (at a rate of about −3 °C/min) cycle of the polymer gels. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer 7 series thermal analysis system under a helium atmosphere at a rate of 10 °C/min.

Results and Discussion

Preparation of Reactive Copolymers. In our experiments, chloromethylstyrene (CMS) and 2-(dimethylamino)ethyl acrylate (DMAEA) were employed as functional monomers; they were copolymerized with styrene (St) and/or butyl acrylate (BA), to obtain the rubberlike BA-St-CMS copolymer (PBSC in Table 1), the BA-DMAEA copolymer (PBN in Table 1), and the plasticlike St-DMAEA copolymer (PSN in Table 1).

Cross-Linking of Chlorine-Containing Polymers. Nine bifunctional tertiary amines were employed as cross-linkers for PCMS and PBSC. Table 2 shows that the CMS (co)polymers could be cross-linked with all the diamines employed. No gelation was, however, observed when the PCMS solution was heated at a relatively high temperature (100 °C) for a long time,

Table 1. Emulsion Polymerization[a]

polymer	monomer ratio (wt/wt)	monomer/H_2O (wt/wt)	KPS/monomer (wt/wt)	temp (°C)	time (h)	yield (%)	MW (by GPC) $10^{-5}M_n$	$10^{-5}M_w$	composition (mol % by ^1H NMR) BA	St	functional unit
PBSC	BA/St/CMS 7.3/8.1/1.0	21.6/100	1.4/100	45	7	95	1.51	7.49	42.8	51.4	5.8 (CMS)
PBN	BA/DMAEA 10.5/1.0	19.2/100	1.6/100	45	8	95	0.42	1.43	94.5		5.5 (DMAEA)
PSN	St/DMAEA 18.9/1.0	26.1/100	0.5/100	40	10	96	0.46	2.02		95.9	4.1 (DMAEA)

[a] 1 wt % (based on water) dodecyl sulfate sodium salt was used as the emulsifier. BA = butyl acrylate; St = styrene; CMS = chloromethylstyrene; DMAEA = 2-(dimethylamino)ethyl acrylate.

Table 2. Cross-Linking and De-Cross-Linking of Polymers Containing CMS Monomeric Unit

no.	polymer[a]	cross-linker[b]	amino/halide (mol/mol)	temp (°C)	gelation time	reaction time (h)	yield (%)	gel %[c]	gel′ %[d]	flowability at 215 °C (Y/N?)
C1	PCMS	no	0	140	no gelation	4				
C2	PCMS	Et_3N	0.2/1	100	no gelation	22				
C3	PCMS	$BzMe_2N$	0.2/1	100	no gelation	22				
C4	PCMS	TMHDA	0.1/1	65	7 min	2	95	100	19	Y
C5	PBSC	DMP	2/1	65	8 h	9	100	100	88	N
C6	PBSC	DPDM	2/1	65	26 h	28	95	100	48	N
C7	PBSC	DPDM	2/1	100	4 h	4	100	100		
C8	PBSC	DPD	2/1	65	24 h	25	97	100	6	Y
C9	PBSC	TMDPD	2/1	65	12 h	13	100	100		Y
C10	PBSC	TMB	2/1	65	32 h	32	96	100	5	Y
C11	PBSC	TMB	2/1	100	4 h	4	100	99		
C12	PBSC	TEEDA	2/1	65	24 h	25	95	100	91	N
C13	PBSC	TEEDA	2/1	100	4 h	4	100	100		
C14	PBSC	TMEDA	2/1	65	3 h	4	99	100	12	Y
C15	PBSC	TMBDA	2/1	65	1 h, 25 min	2	97	100	10	Y
C16	PBSC	TMHDA	2/1	65	50 min	2	98	100	8	Y

[a] PCMS = poly(chloromethylstyrene), 9.5 wt % solution in dimethylformamide (DMF); PBSC = butyl acrylate−styrene−chloromethylstyrene copolymer of Table 1, 6 wt % solution in DMF. [b] TMHDA = tetramethyl-1,6-hexanediamine; DMP = 1,4-dimethylpiperazine; DPDM = dipiperidinomethane; DPD = 2,2′-dipyridyl; TMDPD = 4,4′-trimethylenedipyridine; TMB = tetramethylbenzidine; TEEDA = tetraethylethylenediamine; TMEDA = tetramethylethylenediamine; TMBDA = tetramethyl-1,4-butanediamine. [c] The gel in the cross-linked product. [d] The gel after the cross-linked product together with a mixture of benzyl bromide/dichlorobenzene (1/6 by weight) was heated 4 h in a 190 °C oil bath.

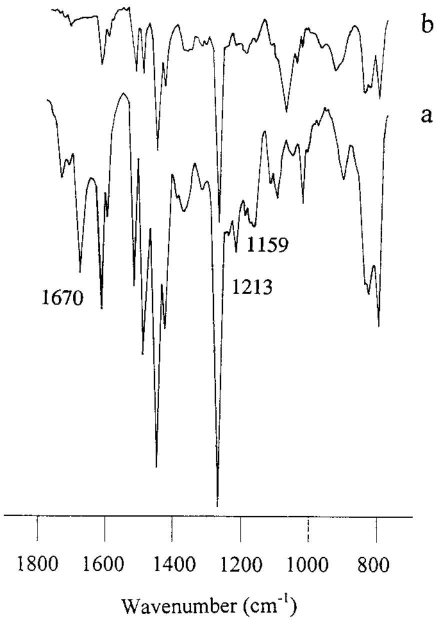


Figure 1. IR spectra of PCMS: (a) cross-linked with TMHDA (C4 in Table 2, KBr tablet); (b) before cross-linking (film).

after a monofunctional tertiary amine was added (C2 and C3 in Table 2), or heated without adding the above amine at a higher temperature (140 °C, C1). Figure 1 presents the IR spectra of the PCMS (b) and its cross-linked product with tetramethyl-1,6-hexanediamine (TMHDA) (a). The peaks at 1670, 1213, and 1159 cm^{-1} can be assigned to the quaternary salt (1640, 1218, and 1154 cm^{-1} were reported in the literature[10]). These results clearly indicate that the gelation was caused by the formation of covalent ionene bridges between the polymer chains and not by the ion pair interactions between the quaternary salt moieties. The cross-linking reactivity was found to depend on the structure of the diamine employed. As shown in Table 2, tetraethylethylenediamine (TEEDA) provided much lower cross-linking reactivity than tetramethylethylenediamine (TMEDA). This was most likely caused by the stronger steric effect of ethyl than methyl groups. The steric effect can also explain the low gelation rate when dipiperidinomethane (DPDM) was used as cross-linker. When 2,2′-dipyridyl (DPD) was employed, the gelation time became twice as large than for 4,4′-trimethylenedipyridine (TMDPD), which contains a flexible trimethylene moiety between its two N atoms. The gelation rate increased with increasing number of methylene groups between the two N atoms of the tetramethyldiamine molecule (no. C14−16 in Table 2). For tetramethylbenzidine (TMB) as cross-linker, which contains a rigid biphenyl group between its two N atoms, the gelation time was very long at 65 °C.

To examine the cross-linkability of Cl-containing polymers with low reactive C−Cl sites, polyepichlorohydrin (PECH, containing primary Cl), poly(vinyl chloride) (PVC, containing secondary Cl), and chlorinated polypropylene (CPP, containing tertiary Cl) were reacted with TMHDA or poly(4-vinylpyridine) (PVP) (Table 3). No gelation of the PVC or PECH solutions

Table 3. Cross-Linking and De-Cross-Linking of Chlorine-Containing Polymers

no.	polymer[a]	cross-linker[b]	temp (°C)	gelation time (h)	reaction time (h)	yield (%)	gel %[c]	gel′ %[d]	flowability at 215 °C (Y/N?)
CL1	CPP	TMHDA	65	no gelation	25				
CL2	CPP	TMHDA	100	12[e]	12	85	98	0	Y
CL3	CPP	PVP	100	14	15	91	92	0	Y
CL4	PECH	TMHDA	65	no gelation	25				
CL5	PECH	TMHDA	100	no gelation	22				
CL6	PECH	PVP	100	14	15	100	78	0	
CL7	PVC	TMHDA	65	no gelation	25				
CL8	PVC	PVP	100	28	28	100	56	0	

[a] CPP = chlorinated polypropylene, 10 wt % solution in the mixed solvent of dimethylformamide (DMF) and toluene (1/2 by volume); PECH = poly(epichlorohydrin), 9 wt % solution in DMF; PVC = poly(vinyl chloride), 9 wt % solution in DMF. [b] TMHDA = tetramethyl-1,6-hexanediamine; PVP = poly(4-vinylpyridine), 10 wt % solution in DMF; amino/halide (mol/mol) was 0.1/1. [c] The gel in the cross-linked product. [d] The gel after the cross-linked product together with a mixture of benzyl chloride/dichlorobenzene (1/6 by weight)was heated 5 h in a 190 °C oil bath. [e] No gelation was observed during the reaction and the obtained mixture gelated when it was cooled to room temperature after reaction.

Table 4. Cross-Linking and De-Cross-Linking of Polymers Containing Tertiary Amino Groups

no.	polymer[a]	cross-linker[b]	halide/amino (mol/mol)	temp (°C)	gelation time	reaction time (h)	yield (%)	gel %[c]	gel′ %	flowability at 215 °C (Y/N?)
N1	PBN	DBX	2/1	65	1 h, 40 min	5	93	100	0[d]	Y
N2	PBN	DCX	2/1	65	10.5 h	16	100	100	0[d]	Y
N3	PBN	DCA	2/1	65	10 h	16	95	100	0[d]	Y
N4	PBN	DBB	2/1	65	no gelation	21				
N5	PBN	DBB	2/1	100	no gelation	19				
N6	PBN	DCB	2/1	65	no gelation	21				
N7	PBN	DCB	2/1	100	no gelation	19				
N8	PSN	DBX	2/1.8	RT[f]	20 min	30	100	96	0[e]	Y
N9	PSN	DCX	2/1.8	60	3.5 h	5	100	98	0[e]	Y
N10	PSN	DCA	2/1.8	60	2 h, 40 min	5	100	87	16[d]	Y
N11	PSN	DBB	2/1.8	60	14 h	17	98	96	0[e]	Y
N12	PSN	DCB	2/1.8	60	no gelation	17				
N13	PSN	DCB	2/1.8	100	no gelation	9				
N14	PSN	BzB	2.4/1	100	no gelation	26				
N15	PVP	DBX	0.1/1	RT[f]	13 min	29	99	100	6[d]	Y
N16	PVP	DCX	0.1/1	60	1 h, 30 min	5	100	99	19[d]	Y
N17	PVP	DCA	0.1/1	60	12 min	5	99	100	28[d]	Y
N18	PVP	DBB	0.1/1	60	1 h, 35 min	5	100	99	86[d]	N
N19	PVP	DCB	0.1/1	60	no gelation	17				
N20	PVP	DCB	0.1/1	100	no gelation	9				
N21	PVP	BzC	0.2/1	100	no gelation	26				
N22	PVP	PCMS	1/1	RT[f]	4 h	96	100	100		

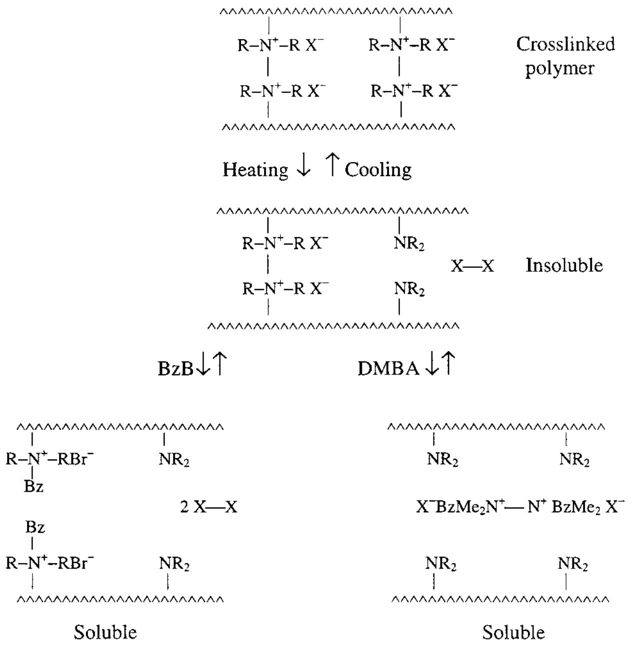
[a] PBN = butyl acrylate−dimethylaminoethyl acrylate copolymer of Table 1, 7 wt % solution in dimethylformamide (DMF); PSN = styrene−(dimethylamino)ethyl acrylate copolymer of Table 1, 7.5 wt % solution in DMF; PVP = poly(4-vinylpyridine), 10 wt % solution in DMF. [b] DBX = α,α′-dibromo-*p*-xylene; DCX = α,α′-dichloro-*p*-xylene; DCA = 1,3-dichloroacetone; DBB = 1,4-dibromobutane; DCB = 1,4-dichlorobutane; BzB = benzyl bromide; BzC = benzyl chloride; PCMS = poly(chloromethylstyrene), 9.5 wt % solution in DMF. [c] The gel in the cross-linked product. [d] The gel after the cross-linked product together with a mixture of dimethylbenzylamine/dichlorobenzene (1/10 by weight) was heated 4 h in a 190 °C oil bath. [e] The gel after the cross-linked product together with a mixture of BzB/benzophenone (1/4 by weight) was heated 2 h in a 210 °C oil bath. [f] RT = room temperature, 24 ± 1 °C.

was observed when they were heated with TMHDA, but partly cross-linked PECH and PVC could be obtained when PVP was used as a multifunctional cross-linker. A high gel % was obtained when CPP was allowed to react with either TMHDA or PVP. The weak carbonium ion character of the secondary and primary C−Cl can be considered responsible for the poor cross-linkabilities of PVC and PECH, since the Menschutkin reaction involves a nucleophilic substitution between an alkyl halide and a tertiary amine.[2]

Cross-Linking of Polymers Containing Tertiary Amine Pendants. Five α,ω-dihalides were employed as cross-linkers for the polymers containing tertiary amine pendant groups, such as BA-DMAEA copolymer (PBN in Table 1), St-DMAEA copolymer (PSN in Table 1), and PVP. As shown in Table 4, the gelation times of PSN and PVP were 20 (N8) and 13 min (N15), respectively, at room temperature (ca. 24 °C), for α,α′-dibromo-*p*-xylene (DBX) as cross-linker, indicating a high cross-linking reactivity of this dihalide. No gelation was reached, however, when PSN and PVP were reacted with a monohalide, such as benzyl bromide (BzB, N14) and benzyl chloride (BzC, N21), respectively, at large halide/amine mole ratios and a high temperature (100 °C) for as long as 26 h. These results clearly indicate that the formation of covalent ionene bridges and not the ion pair interactions was responsible for the cross-linking of these polymers. No gelation was, however, observed for 1,4-dichlorobutane (DCB) as cross-linker, indicating a low reactivity of the primary chlorine of the DCB. As expected, the cross-linking reactivity decreased in the carbonium ion character sequence DBX > DCA > DCX > DBB > DCB.

Thermal De-Cross-Linking/Re-Cross-Linking of the Networks Generated with Polymers Containing Tertiary Amine Pendants. The cross-linked polymers were insoluble even on heating in pure dichlorobenzene or benzophenone. However, they could be dissolved at least partially after heated in the same solvent containing dimethylbenzylamine (DMBA) or benzyl bromide (BzB) (Table 4). As shown in Scheme 2, when the polymer was heated in the pure solvent, the

Scheme 2



thermodynamic equilibrium between dequaternization and quaternization allowed some of the ionene bridges to remain, and this kept the polymer insoluble. The addition of BzB or DMBA to the solvent displaced, however, the equilibrium in the direction of dequaternization, resulting in an enhanced dissociation of the polymer.

The flowability, which constitutes an effective indication of de-cross-linking on heating, was investigated by thermocompression (heating/cooling compression cycle). A cross-linked polymer was regarded as thermally flowable when (1) a continuous, transparent thin film of about 0.2 mm in thickness could be obtained after each of the successive thermocompression cycles and (2) the film did not dissolve or crack into small gel pieces when it was submerged into dimethylformamide (DMF) immediately after each compression cycle. As shown in Table 4, all cross-linked polymers except PVP cross-linked with 1,4-dibromobutane (DBB, N18) exhibited good flowability on heating during compression. No notable change in the flowability was observed even after five cycles when the PSN cross-linked with 1,3-dichloroacetone (DCA, N10) or DBB (N11) was subjected to five successive thermocompressions. The film thus obtained was found to merely swell when introduced in DMF immediately after the fifth cycle. However, the PVP film, cross-linked with DCA (N17), could dissolve in DMF after the fifth cycle, indicating that no re-cross-linking occurred during the cooling stage of the fifth cycle. Most likely the DCA, generated via dequaternization, escaped from the system because the heating temperature (215 °C) was much higher than its boiling point (173 °C). The thermocompression and swelling experiments indicated that the de-cross-linking during heating and re-cross-linking during cooling were rapid, the former lasting about 10 min and the latter about 15 min.

To investigate the effect of the structure of the reactants on the reversible conversion of the ionene network, it is useful to examine the mechanism of dissociation of the ionene bridges. Generally, several competitive reactions may occur during dequaternization of an ammonium salt because an alkyl halide can be generated from the halide anion X^- and any one of the four alkyl groups (in the present case two bridging and two nonbridging alkyls) connected with each of the nitrogen atoms. Of course, the competitive reactions that result in the generation of nonbridging alkyl halides could not induce the dissociation of the network. Two factors ensure that the dequaternization will lead to the de-cross-linking of the polymer. First, the tension that exists along the linking bridges, especially when the network is subjected to shear stress, enhances the likelihood of dequaternization via the dissociation of the bridges. Second, the reverse Menschutkin reaction as well as its forward reaction involve the formation of a carbonium ion in the transition state. The alkyl that generates the strongest carbonium ion in the transition state will dissociate prior to the other three alkyls, resulting in the corresponding alkyl halide and tertiary amine. Indeed, only the alkyl that possessed the higher carbonium ion strength dissociated during the dequaternization of ammonium salts.[2b,c] Consequently, for the dissociation of the ionene network to occur during the dequaternization of the cross-linked PSN and PBN, the bridging alkyls should possess greater carbonium ion strength than the nonbridging ones. The cross-linked DMAEA containing polymers can dissociate in two ways, with the formation of either $-OCH_2CH_2-$halide (and the corresponding Me_2N-) or $-OCH_2CH_2-NMe_2$ (and the corresponding halide of the cross-linker). In contrast, the de-cross-linking of the cross-linked PVP can occur only through the formation of the stable aromatic pyridine group and the corresponding halide cross-linker. However, the carbonium ion strength of butylene is lower than that of benzyl, and this constitutes most likely the reason for the high gel′ % (86%) and poor flowability of the DBB cross-linked PVP (N18 in Table 4).

A side reaction that might occur is the Hoffmann degradation. Indeed, traces of the Hoffmann degradation products were detected even when a diamine and a dihalide were polymerized at room temperature.[11] In addition, the mass spectrometry of the pyrolysis of tetraalkylammonium bromides indicated that the intensity of $[HBr]^+$ ions (one of the degradation products) was 0.2−2.6% (mostly <1%) of the total ion current (ion source temperature 210−230 °C).[12] The Hoffmann degradation might be one of the side reactions during the dequaternization of the cross-linked polymers that possess βH in their ammonium moieties. Such a degradation and the subsequent irreversible changes of the generated C=C bonds might result in irreversible cross-linking.

The IR and ^{1}H NMR spectra of DCA and DBB cross-linked PSN (N10 and N11 in Table 4) were recorded before and after the thermocompression cycles. Figure 2 presents the IR spectra of the non-cross-linked PSN (a) and DBB cross-linked ones, before (b) and after five compression cycles (c). The peak at 1159 cm^{-1} can be assigned to $-NMe_2$ of the DMAEA functional monomeric unit (1164.5 cm^{-1} in the literature[13]), the peak at 1244 cm^{-1} to the quaternary ammonium moieties (1244.2 cm^{-1} in the literature[14]) of the generated ionene bridges, and the peak at 1263 cm^{-1} to the unreacted $-CH_2Br$ groups (1260.6 cm^{-1} in the literature[15]). Spectra b and c and their differential (Figure 2d) indicate that almost no detectable change in the polymer chain structure occurred after the polymer was subjected to

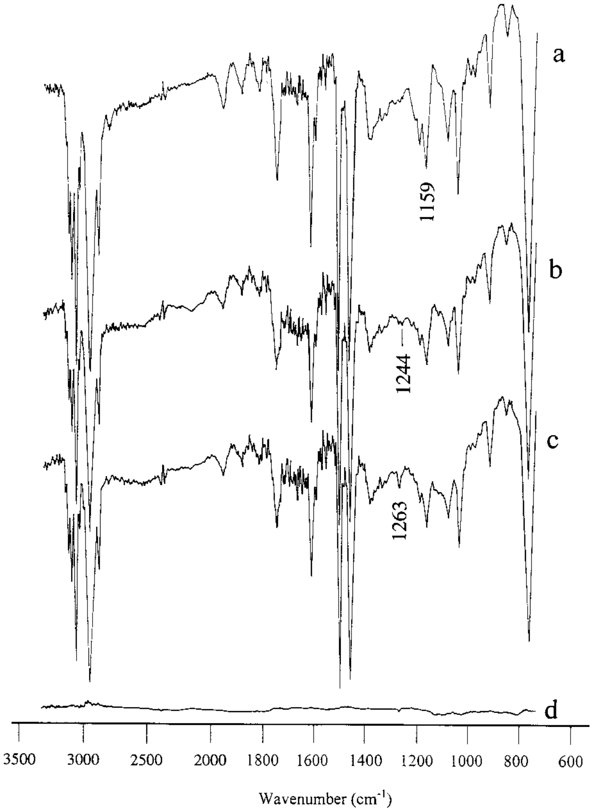


Figure 2. IR spectra of PSN (KBr tablet): (a) without cross-linking (PSN in Table 1); (b) cross-linked with DBB (N11 in Table 4); (c) polymer N11 in Table 4 after five thermocompression cycles; (d) differential spectrum of the polymer N11 (c−b).

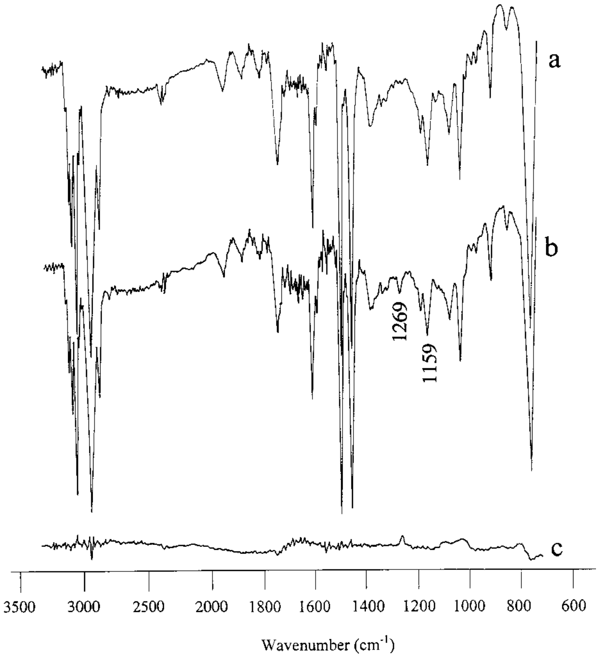


Figure 3. IR spectra of DCA cross-linked PSN (N10 in Table 4, KBr tablet): (a) before any thermocompression; (b) after five thermocompression cycles; (c) differential spectrum (a−b).

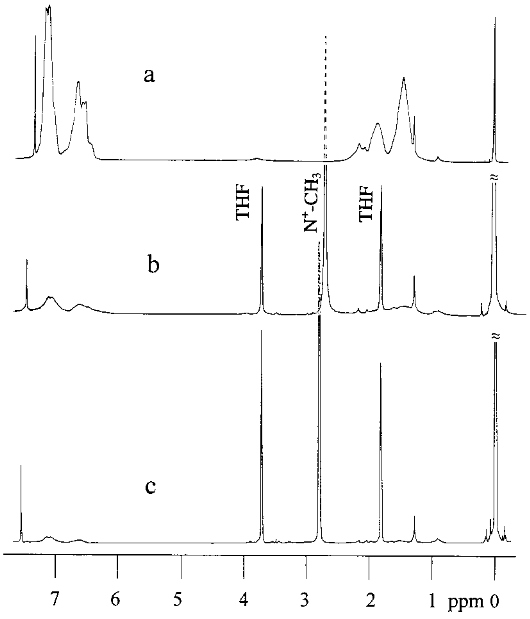


Figure 4. ^{1}H NMR spectra of PSN: (a) without cross-linking (PSN in Table 1), recorded in DCCl$_3$; (b) cross-linked with DBB (N11 in Table 4), recorded in DCCl$_3$/THF-d_8 (7/3 by volume); (c) polymer N11 in Table 4 after five thermocompression cycles, recorded in DCCl$_3$/THF-d_8 (7/3 by volume).

five compression cycles. The −CH$_2$Br peak (1263 cm^{-1}) became somewhat stronger, indicating that some of the −CH$_2$Br groups generated via dequaternization on heating did not requaternize during the cooling stage of the cycles. A similar conclusion was obtained from the spectra recorded for DCA cross-linked PSN, before (Figure 3a) and after five compression cycles (Figure 3b) and their differential (Figure 3c). In the latter case, the peak at 1269 cm^{-1} can be assigned to the unreacted −CH$_2$Cl groups of DCA (1260 cm^{-1} in the literature[16]).

The ^{1}H NMR spectra of the cross-linked PSN were recorded by dispersing and swelling polymer powders in a solvent mixture of DCCl$_3$ and THF-d_8 (about 7/3 by volume). Figure 4 presents the ^{1}H NMR spectra of the non-cross-linked PSN (a) and the DBB cross-linked ones, before (b) and after five compression cycles (c). The peak at 2.7−2.8 ppm can be assigned to the N$^+$CH$_3$ groups of the ionene bridges.[17,18] This peak remained strong even after the polymer was subjected to five compression cycles. The ^{1}H NMR spectra of DCA cross-linked PSN before (Figure 5a) and after five compression cycles (Figure 5b) provided the same conclusion as the DBB cross-linked PSN. However, quantitative calculations based on NMR data could not be carried out, because of the inconsistency between the peak intensities and the number of the corresponding H atoms. This inconsistency was caused by the heterogeneity of the tested powder dispersions. Nevertheless, the obtained ^{1}H NMR spectra provide an indication that the ionene bridges were regenerated after the thermocompression cycles.

Thermal De-Cross-Linking/Re-Cross-Linking of the Networks Generated with Chlorine-Containing Polymers. The thermal reversibility of the cross-linked Cl-containing polymers was investigated via reactive solubility and thermocompression. As shown in Tables 2 and 3, all the cross-linked polymers, except PBSC cross-linked with 1,4-dimethylpiperazine (DMP), dipiperidinomethane (DPDM), or tetraethylethylenediamine (TEEDA) (C5, C6, and C12, respectively, in Table 2), could be almost completely dissolved in dichlorobenzene containing BzB or BzC and exhibited flowability on heating. Insoluble, continuous, and transparent thin films were obtained from PBSC cross-linked with 2,2′-dipyridyl (DPD), 4,4′-trimethylenedipyridine (TMDPD), or tetramethyl-1,4-butanediamine (TMBDA), even when

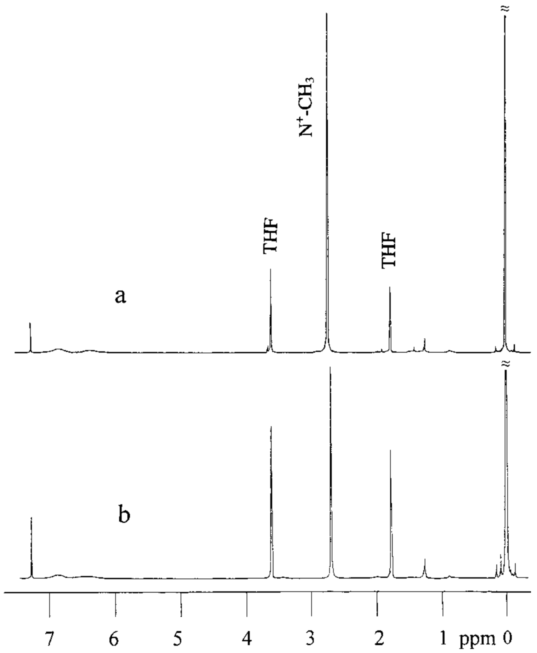
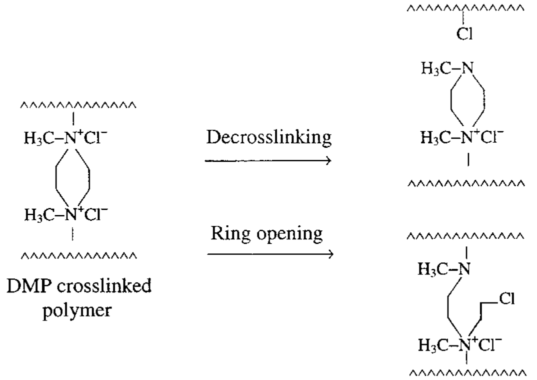


Figure 5. ^{1}H NMR spectra of DCA cross-linked PSN (N10 in Table 4), recorded in DCCl$_3$/THF-d_8 (7/3 by volume): (a) before any thermocompression; (b) after five thermocompression cycles.

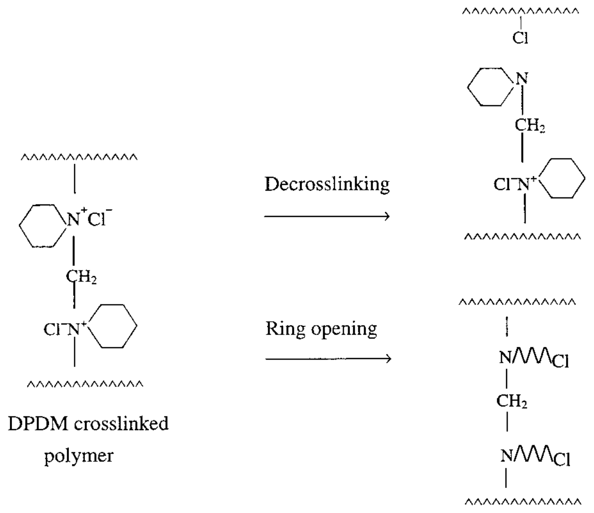
Scheme 3



they were subjected to five thermocompression cycles.

With DMP, DPDM, and TEEDA as cross-linkers, high insoluble fractions (gel$'$ %) were found after reactive solubility experiments were carried out with the cross-linked PBSC. No continuous films could be obtained by the thermocompression of the three cross-linked polymers. Furthermore, the compressed samples cracked into small gel particles when they were submerged into DMF. The poor reversibilities of the above three cross-linked polymers were probably due to a variety of reasons. Because of the tension in the ring, the reverse Menschutkin reaction might have occurred in a ring-opening way that did not dissociate the network generated by DMP (Scheme 3) or DPDM (Scheme 4). When the TEEDA cross-linked polymer was subjected to heating, a competitive reaction that generated ethyl chloride from either of the two nonbridging ethyl groups might have resulted in an incomplete dissociation of the network, since the nonbridging ethyl groups of TEEDA possess a carbonium ion strength comparable to that of the bridging-ethylene group. Additionally, the Hoffmann degradation might have occurred since there are at least two alkyl groups that possess βH in each of the amine moieties of DMP, DPDM, and TEEDA.

Scheme 4



Conductivity Investigations of the Polymer System during Cross-Linking and De-Cross-Linking. When the conductivity of the PBSC/PBN mixture in benzophenone (CM4 in Table 5) was determined at 100 °C, it increased from $6/\delta$ μS/cm (where δ ca. 0.3 cm is the thickness of the solution layer) to $13/\delta$ μS/cm during the first hour, to $24/\delta$ μS/cm after an additional 3 h, after which it remained constant. A different time dependence was recorded when a PCMS solution contained a high concentration of PVP (CM2 in Table 5) or TMHDA (CM3 in Table 5). Indeed, Figure 6 shows that the conductivity of the PCMS solution remained almost unchanged in the absence of a cross-linker (CM1 in Table 5, curve B). However, the conductivity of the solution of PCMS and PVP (curve A) increased sharply at the beginning, due to the formation of ionene ion pairs, and decreased after a maximum was attained. A maximum in the conductivity was also attained (curve C) when the cross-linker TMHDA was introduced into the PCMS solution. The decrease in the conductivity might be the result of the formation of a network with an increasing cross-link density which caused an increasing resistance to the motion of the generated ions. These conductivity results provided additional evidence that the cross-linking of the polymer was caused by the quaternization between the halide and the tertiary amine.

The conductivity of the cross-linked polymer mixtures (polymer gels, Table 5) was determined at various temperatures. Figure 7 presents the temperature dependence of the conductivity recorded during a cycle of heating (curve B) and cooling (curve C) of a PCMS/PVP gel. The conductivity increased with increasing temperature from 90 to 130 °C and 170 to 205 °C but remained almost unchanged in the temperature range 130−170 °C by decreasing little with rising temperature. A low increase of the conductivity was recorded when a PCMS solution free of cross-linker was heated under the same conditions (curve A). Obviously, the range of temperatures in which the conductivity remained almost constant was a result of the competition between the reduction of the number of ion pairs due to the dequaternization of the ionene bridges with increasing temperature and the increase of the conductivity with increasing temperature. The conductivity returned to its original level when after the heating of PCMS/PVP gel the system was cooled to 90 °C. In other words, the dequaternized ionene moieties were regenerated rapidly

Table 5. Cross-Linking Systems for Conductivity Measurements

no.	Cl-containing polymer[a]	cross-linker or amino-containing polymer[b]	amino/chlorine (mol/mol)	solvent[c]	polymer concn (wt %)	heating time at 100 °C (h)
CM1	PCMS	no	0/1	1-chloro-2-nitrobenzene	14	1
CM2[d]	PCMS	PVP	1/1	1-chloro-2-nitrobenzene	10	1
CM3[d]	PCMS	TMHDA	1/1	1-chloro-2-nitrobenzene	14	4
CM4[d]	PBSC	PBN	1/1	benzophenone	11	5

[a] PCMS = poly(chloromethylstyrene); PBSC = butyl acrylate−styrene−chloromethylstyrene copolymer of Table 1. [b] PVP = poly(4-vinylpyridine); TMHDA = tetramethyl-1,6-hexanediamine; PBN = butyl acrylate−(dimethylamino)ethyl acrylate copolymer of Table 1. [c] Containing 0.3 wt % TBC. [d] Gelation was observed after the heating.

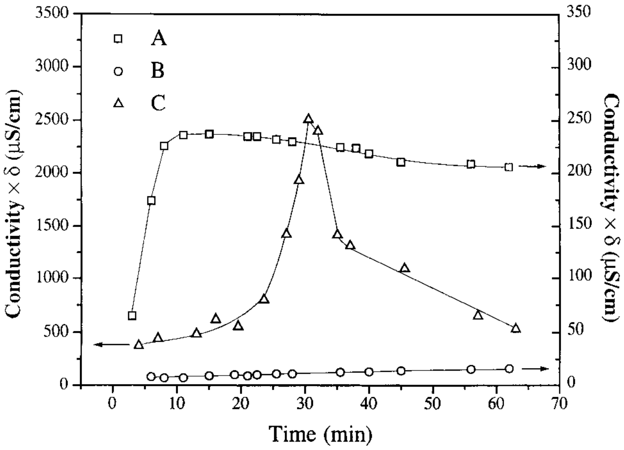


Figure 6. Conductivity of polymer mixtures recorded at 100 °C: (A) PCMS/PVP solution (CM2 in Table 5); (B) PCMS solution (CM1 in Table 5); (C) PCMS/TMHDA solution (CM3 in Table 5). δ (ca. 0.3 cm) is the thickness of the solution layer.

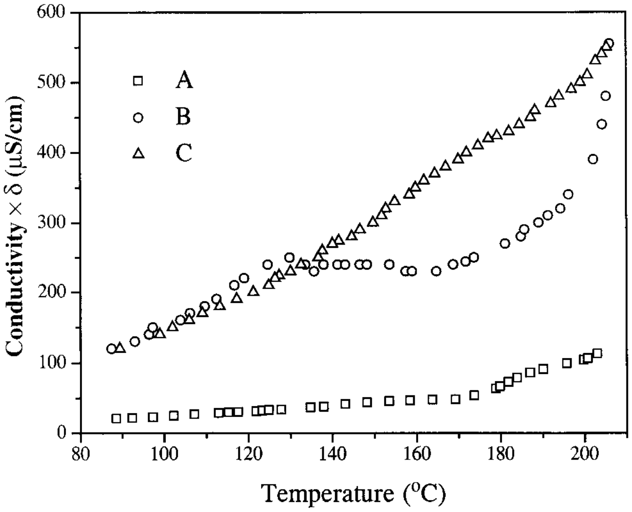


Figure 7. Temperature dependence of the conductivity of (A) PCMS solution (CM1 in Table 5); (B) PCMS/PVP gel (CM2 in Table 5), recorded during the heating stage; and (C) the same gel as (B), recorded during the cooling stage. δ (ca. 0.3 cm) is the thickness of the gel layer.

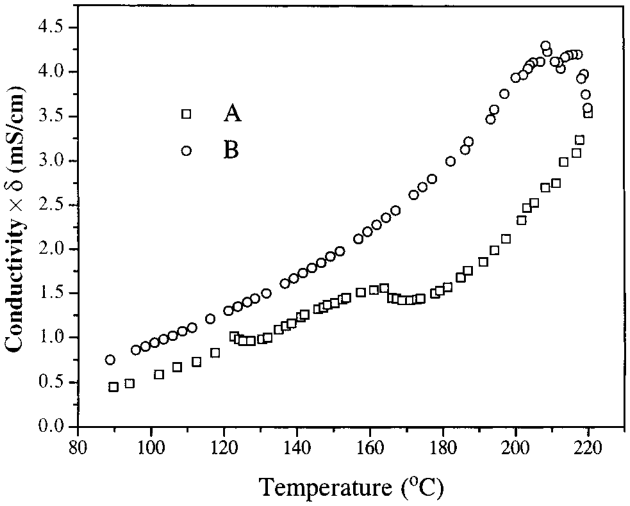


Figure 8. Temperature dependence of the conductivity of PCMS/TMHDA gel (CM3 in Table 5): (A) recorded during the heating stage; (B) recorded during the cooling stage. δ (ca. 0.3 cm) is the thickness of the gel layer.

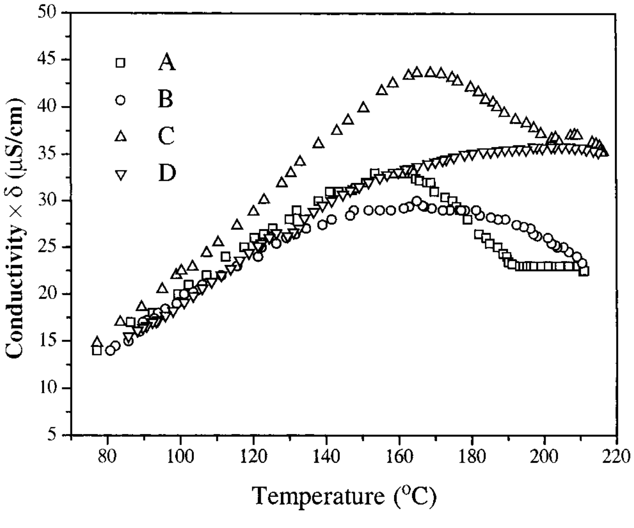


Figure 9. Temperature dependence of the conductivity of PBSC/PBN gel (CM4 in Table 5): (A) recorded during the heating stage of the first cycle; (B) recorded during the cooling stage of the first cycle; (C) recorded during the heating stage of the second cycle; (D) recorded during the cooling stage of the second cycle. δ (ca. 0.3 cm) is the thickness of the gel layer.

during the cooling period. A similar conductivity−temperature relationship was observed when the PCMS/TMHDA gel was subjected to the heating and cooling cycle (Figure 8). In this case, the conductivity remained almost constant during heating between 123 and 130 °C and between 165 and 170 °C.

An interesting result was observed when the PBSC/PBN gel, which possessed a lower cross-link density in its network than PCMS/PVP and PCMS/TMHDA, was subjected to the heating/cooling cycles. As shown in Figure 9, the conductivity increased from 80 to 160 °C and decreased with a further rise in temperature (curve A). This probably occurred because at a temperature greater than 160 °C the increase in conductivity due to the temperature was less than the decrease in conductivity caused by dequaternization. During cooling (curve B), the conductivity increased when the temperature was lowered from 213 to 165 °C and acquired exactly the starting level at the end of the cycle. After the polymer gel was cooled to room temperature and kept for about 24 h at the latter temperature, it was subjected

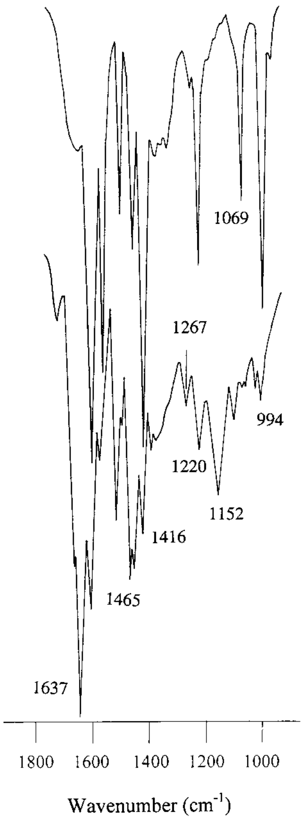


Figure 10. IR spectra of PVP: (a) cross-linked with PCMS (N22 in Table 4, KBr tablet); (b) before cross-linking (KBr tablet).

to a second heating/cooling cycle. As during the first cycle, the conductivity decreased after 165 °C (curve C) during the heating stage. The two heating/cooling cycles provided similar behaviors regarding the change in conductivity. There were, however, large differences at the high temperatures, which indicated that the process was not completely reversible. The conductivity measurements provided evidence that the dequaternization occurred through dissociation of the covalent ionene bridges, almost free of CH_3Cl formation (through the dequaternization of the nonbridging methyl groups). Indeed, otherwise, the conductivity could not have returned to its original level, because CH_3Cl having a low boiling point (−24.2 °C) would have escaped from the liquid phase and requaternization could not have occurred.

DSC Analysis. The thermal analysis of dequaternization is expected to provide some information about the reversibility of the ionene network. Therefore, the cross-linked PCMS/PVP system (N22 in Table 4) which contains a large number of ion pairs was subjected to the DSC test, after its structure was confirmed by the IR spectrum. Compared to the spectra of PVP (Figure 10b) and PCMS (Figure 1b), the peaks at 994, 1069, 1220, and 1416 cm^{-1}, which can be assigned to PVP,[19] and the peak at 1267 cm^{-1}, which is the characteristic absorption peak of chloromethylene of PCMS,[20] are relatively weak in the spectrum of the cross-linked PCMS/PVP (Figure 10a). The strong peaks at 1152, 1465, and 1637 cm^{-1}, which can be assigned to the quaternary salt of pyridine,[21] indicate that a covalent network of PCMS/PVP was generated by the quaternization between the chloromethylene group of PCMS and the pyridine ring of PVP.

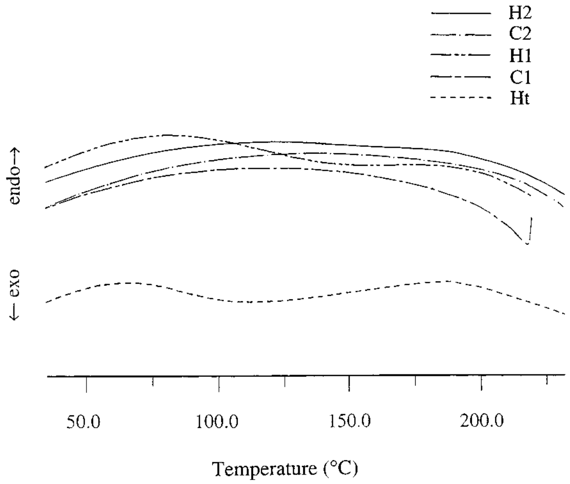


Figure 11. DSC curves of PVP cross-linked with PCMS (N22 in Table 4): (H1) recorded during the heating stage of the first cycle; (C1) recorded during the cooling stage of the first cycle; (H2) recorded during the heating stage of the second cycle; (C2) recorded during the cooling stage of the second cycle; (Ht) recorded during the heating stage after the polymer was heated at 220 °C for 7 min, cooled to 110 °C and kept at 110 °C for 2 h, and finally cooled to room temperature. All DSC tests were carried out under a helium atmosphere, at a heating rate of 10 °C/min and a cooling rate of −10 °C/min.

Figure 11 presents the DSC curves recorded during a first heating (H1) and cooling (C1) and a second heating and cooling (H2 and C2) (carried out immediately after the first one). Nonstraight curves were recorded for both the heating and cooling stages of the two cycles because of the change of the specific heat of quaternary salts with temperature.[9] An anomalous thermal transition peak can be seen at 145−150 °C in curve H1. As reported by Burns et al.,[9] the decomposition temperature of a quaternary ammonium salt is characterized by a broad and symmetrical thermal transition. Such broad thermal transition peaks were also observed for the ionene polyelectrolytes.[3a,23] The peak observed in Figure 11 is located in the range (130−170 °C) in which the conductivity of the PCMS/PVP gel remained almost constant during heating. Consequently, this peak can be attributed to the thermal transition during the dequaternization of the PCMS/PVP ionene network. No thermal transition can be noted in the cooling curves (C1 and C2) of the first and second cycle, and only a small change in curvature can be noted around 150 °C in the heating curve (H2) of the second cycle. The above curves indicated that after the first dequaternization the polymer remained almost in the same state during the first cooling, the second heating, and the second cooling. This occurred because both polymers have high glass transition temperatures, and hence their segments have low mobilities. However, after the treatment described below, a thermal transition similar to that observed during the first heating could be detected. The polymer was wrapped in an aluminum foil and heated at 220 °C for 7 min, was cooled in 10 min to 110 °C (a temperature close to the glass transition temperatures of PCMS and PVP) at which it was kept for 2 h in order to stimulate the thermal motion of the segments of PCMS and PVP chains, and finally was cooled to room temperature. As shown by curve Ht in Figure 11, a thermal transition peak which started at about 70 °C and ended at about 190 °C was present in a somewhat different temperature range than for curve H1, indicating that the ionene network was regenerated during the cooling program employed.

Conclusion

The results obtained from the cross-linking reactions, IR and ^{1}H NMR tests, reactive solubility experiments, thermocompression cycles, conductivity measurements, and DSC indicated that covalent networks could be obtained via the formation of ionene bridges between polymer chains and that such networks exhibited thermally reversible cross-linking due to quaternization on cooling and dequaternization on heating. The cross-linking reactivity and thermal de-cross-linking/re-cross-linking behavior were markedly affected by the structures of the two kinds of functional groups involved in the quaternization, the tertiary amine, and halide−carbon groups. Reversibility can be achieved if (among the alkyl groups connected to the N atoms) the bridging alkyl groups provide an enough high carbonium ion strength compared to those of the nonbridging alkyl groups and if no or few βH are present in the ammonium salt moieties to initiate the Hoffmann degradation. The polymers containing a functional monomeric unit, such as chloromethylstyrene, 2-(dimethylamino)ethyl acrylate, and vinylpyridine, could be quaternized effectively with selected cross-linkers under moderate conditions to generate ionene networks that exhibited thermal reversibility.

References and Notes

(1) (a) Rembaum, A.; Baumgartner, W.; Eisenberg, A. *J. Polym. Sci., Polym. Lett.* **1968**, *6*, 159. (b) Somoano, R.; Yen, S. P. S.; Rembaum, A. *J. Polym. Sci., Polym. Lett.* **1970**, *8*, 467. (c) Noguchi, H.; Rembaum, A. *Macromolecules* **1972**, *5*, 253. (d) Rembaum, A.; Noguchi, H. *Macromolecules* **1972**, *5*, 261. (e) Hadek, V.; Noguchi, H.; Rembaum, A. *Macromolecules* **1971**, *4*, 494.

(2) (a) Leffek, K. T.; Matheson, A. F. *Can. J. Chem.* **1972**, *50*, 986. (b) Ko, E. C. F.; Leffek, K. T. *Can. J. Chem.* **1972**, *50*, 1297. (c) Ko, E. C. F.; Leffek, K. T. *Can. J. Chem.* **1970**, *48*, 1865. (d) Burns, J. T.; Leffek, K. T. *Can. J. Chem.* **1969**, *47*, 3725. (e) Leffek, K. T.; Tsao, F. H. C. *Can. J. Chem.* **1968**, *46*, 1215. (f) Gordon, J. E. *J. Org. Chem.* **1965**, *30*, 2760.

(3) (a) Prasad, B. B.; Easo, S.; Kumar, A. *Polym. J.* **1994**, *26* (3), 251. (b) Yano, S.; Tadano, K.; Jerome, R. *Macromolecules* **1991**, *24*, 6439. (c) Klun, T. P.; Wendling, L. A.; Van Bogart, J. W. C.; Robbins, A. F. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 87. (d) Grassl, B.; Galin, J. C. *Macromolecules* **1995**, *28*, 7035.

(4) (a) Dieterich, D.; Keberle, W.; Witt, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9* (1), 40. (b) Watanabe, M.; Takizawa, Y.; Shinohara, I. *Polymer* **1983**, *24*, 491. (c) Loveday, D.; Wilkes, G. L.; Bheda, M. C.; Shen, Y. X.; Gibson, H. W. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32* (1), 1. (d) Ikeda, Y.; Murakami, T.; Yuguchi, Y.; Kajiwara, K. *Macromolecules* **1998**, *31*, 1246.

(5) (a) Dieterich, D.; Bayer, O.; Peter, J.; Muller, E. *DBP* 1156977, 1962. (b) Wieden, H.; Rellensmann, W.; Dieterich, D.; Nischk, G. E. Brit. Pat. 1150634, 1965. (c) Dolezal, T.; Edwards, D. C.; Wunder, R. H. *Rubber World* **1968**, *158*, 46. (d) Buckler, E. J.; Briggs, G. J.; Dunn, J. R.; Lasis, E.; Wei, Y. K. *Rubb. Chem. Technol.* **1978**, *51*, 872. (e) Rutkowska, M. *J. Appl. Polym. Sci.* **1986**, *31*, 1469.

(6) (a) Engle, L. P.; Wagener, K. B. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1993**, *C33* (3), 239. (b) Wagener, K. B.; Engle, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 865.

(7) (a) Leir, C. M.; Stark, J. E. *J. Appl. Polym. Sci.* **1989**, *38*, 1535. (b) Feng, D.; Venkateshwaran, L. N.; Wilkes, G. L.; Leir, C. M.; Stark, J. E. *J. Appl. Polym. Sci.* **1989**, *38*, 1549.

(8) (a) Craven, J. M. U. S. Pat. 3435003, 1969. (b) Takeshita, Y.; Uoi, M.; Hirai, Y.; Uchiyama, M. Ger. Pat. 2164022, 1972. (c) Harumi, A.; Shyuzo, K. Jpn. Pat. 48-36293, 1973. (d) Kennedy, J. P.; Castner, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2055. (e) Salamone, J. C.; Chung, Y.; Clough, S. B.; Watterson, A. C. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2923. (f) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules*, **1990**, *23*, 2636. (g) Canary, S. A.; Stevens, M. P. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1755. (h) Jiao, S. K.; Bing, J. L.; Li, X. Y. *Acta Polym. Sin.* **1994**, *6*, 702. (i) Chen, X. N.; Ruckenstein, E. *J. Polym. Sci., Polym. Chem. Ed.* **1999**, *37*, 4390. (j) Ruckenstein, E.; Chen, X. N. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 818. (k) Chen, X. N.; Jiao, S. K. *Acta Polym. Sin.* **1999**, *5*, 564. (l) Fawcett, A. H.; McGonigle, E.; Hohn, M.; Russell, E. *Polym. Prepr.* **1999**, *40* (1), 232.

(9) Burns, J. A.; Verrall, R. E. *Thermochim. Acta* **1974**, *9*, 277.

(10) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 1, pp 1320B and 1322A.

(11) Wang, J.; Meyer, W. H.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *185*, 1777.

(12) Verrall, R. E.; Burns, J. A. *Can. J. Chem.* **1974**, *52*, 3438.

(13) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; p 168. (b) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 1, p 675C.

(14) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 1, p 1322C.

(15) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 1, p 74D.

(16) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 1, p 417A.

(17) (a) Noguchi, H.; Rembaum, A. *Macromolecules* **1972**, 5, 253. (b) Noguchi, H.; Rembaum, A. *J. Polym. Sci., Polym. Lett.* **1969**, 7, 383. (c) Rembaum, A.; Singer, S.; Keyzer, H. *J. Polym. Sci., Polym. Lett.* **1969**, 7, 395. (d) Chen, X. N.; Ruckenstein, E. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(18) When the ^{1}N NMR spectrum of a linear ionene was recorded using its solution in D_2O, a normal peak of the N^+CH_3 was present at 3.1 ppm. However, when the solvent, D_2O, was replaced by the mixture of $DCCl_3$/THF-d_8, a nonsolvent for ionene, the chemical shift of the N^+CH_3 became 2.8 ppm and the intensity of this peak became abnormally strong.[17d]

(19) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 2, pp 1209 and 1223.

(20) Hoffenberg, D. S. *Ind. Eng. Chem., Prod. Res. Dev.* **1964**, *3* (2), 113.

(21) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chem. Co.: Milwaukee, 1985; Vol. 2, pp 731 and 757.

(22) Gordon, J. E. *J. Org. Chem.* **1965**, *30*, 2760.

(23) The broad thermal transition is the result of the low starting temperature and high completing temperature of dequaternization. The dequaternization of ammonium salts can start at a temperature below 100 °C.[22]

MA0006272