

Cationic quaternary polyelectrolytes based on dialkylaminoisoprenes

Cesar Liberato Petzhold¹, Josemar Stefens¹, Luciane Lemos Monteavaro¹, Reimund Stadler^{2,*}

¹ Universidade Federal do Rio Grande do Sul, Instituto de Química, Av. Bento Gonçalves 9500, Porto Alegre, Brazil

² Universität Bayreuth, Makromolekulare Chemie II, 95440 Bayreuth, Germany

Received: 29 December 1999/Revised version: 23 March 2000/Accepted: 31 March 2000

Summary

Cationic polyelectrolytes were obtained from anionic synthesis of poly[5-(N,N-dialkylamino)isoprene]s by quaternization of the tertiary amino group. The reaction takes place easily using dimethyl sulfate as alkylating agent. The quaternized polymers are completely water-soluble and were characterized by NMR spectroscopy. An application of this material as phase transfer catalyst in the polymerization of 4-bromo-2,6-dimethyl phenol was also demonstrated.

Introduction

Ionic polymers represent a broad class of polymers with charged groups attached to their chains. When the content of these charged groups is very high, the polymers are generally water-soluble and are described as polyelectrolytes.

Polyelectrolytes are classified into three main groups - anionic, cationic and zwitterionic - depending on the nature of the residual charge in aqueous solution. One of the most versatile and useful type of polyelectrolytes is the cationic, of which the polymers containing quaternized amino groups, called polyquats, are the most important class, although non-nitrogen-based cationic species, as polysulfonium and polyphosphonium salts are also known.(1-3)

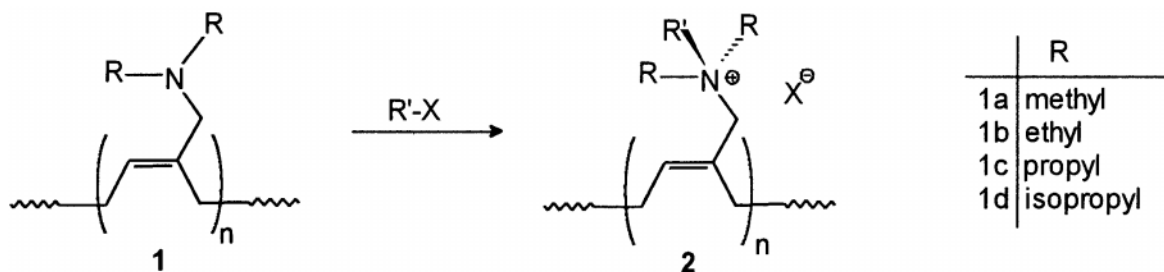
Polyamines and polyquats are mainly prepared by free radical, by ring opening polymerization, by condensation polymerization, and by reactions on the polymer backbone.(4) Only a few examples of polyamines synthesized by anionic chain polymerization are described in the literature, e.g. polyvinylpyridine.(5)

Recently, we reported the first experiments of the anionic polymerization of N,N-dialkyl-2-vinylallylamines [trivial names: 5-(N,N-dialkylamino)isoprenes, 2-[(N,N-dialkylamino)methyl]-1,3-butadiene], functionalized 1,3-dienes. (6-8) The homopolymerization of aminoisoprenes can only be performed in non-polar solvents at low temperatures using alkyl-lithium as initiator. Otherwise, the conversion will not be quantitative. The polymerization occurs by a 4,1-addition of the monomer to the end of the anionic chain and the

* Deceased June 14, 1998

polymer microstructure depends on the bulkiness of the tertiary amino group as well as on the solvent used.

Through quaternization of the tertiary amino groups of poly(dialkylaminoisoprenes) a new class of cationic polyelectrolytes can be obtained. (Scheme 1)



Scheme 1

The present paper reports the preparation and characterization of quaternized poly[5-(N,N-dialkylamino)isoprene]s (1a-d) and also their application as phase transfer catalysts in the polymerization of poly(2,6-dimethyl-1,4-phenylenether), (PPO).

Experimental

Polymerization

Monomers and solvents were purified as described elsewhere.⁽⁹⁾ Anionic polymerizations were performed under argon atmosphere. Before the polymerization, the reaction vessel was heated to 200°C under high vacuum and then purged with argon. After solvent condensation, the initiator sec-butyllithium (1.3 M solution in cyclohexane/hexane, Aldrich) was added to the reaction vessel at -40°C and subsequently the purified monomer. After 3-4 hours the polymerization was terminated by addition of degassed methanol. The polymer was precipitated in acetone or ethanol and dried under reduced pressure.

Quaternization

The reaction was carried out at room temperature in a mixture of (1:3) methanol and benzene. The polymer was dissolved in benzene and then methanol was added to the solution until it turned cloudy. The polymer should not precipitate at this point. The alkylating reagent (dimethyl sulfate) was then added, and the mixture was stirred for a definite reaction time until it turned clear again. The quaternized polymer was precipitated in diethyl ether and dried under vacuum.

Phase transfer polymerization

4-bromo-2,6-dimethylphenol (BDMP) was prepared according to the literature procedure.⁽¹⁰⁾ BDMP (3.3 mmol) was dissolved into 5.4 mL of 6N NaOH with rapid stirring. Afterwards 5.4 mL toluene were added followed by 0.165 mmol of the phase transfer polymer catalyst. During the reaction, air was bubbled through the solution. After 12

hours, the polymerization was quenched by addition of 6N HCl until neutrality was reached. The toluene layer was separated and the polymer was precipitated into methanol, filtered and dried under vacuum.

Structural characterization

$^1\text{H-NMR}$ (200MHz) spectra were recorded on a Varian VX200 spectrometer in deuterated chloroform or deuterium oxide at room temperature.

Size exclusion chromatography was performed in THF as eluent on a Waters GPC equipped with a differential refractometer detector and PS/DVB columns (Waters Styragel). A calibration curve with polystyrene standard was used.

Static light scattering was performed on a standard setup (BI-200M goniometer, He-Ne laser (Spectra Physics), $\lambda = 632.8$ nm) in cyclohexane at room temperature. The refractive index increment (dn/dc) was obtained from the refractive index of polymer solutions (concentration range: 200 to 5 mg/ml) measured in an Abbe refractometer adapted to a laser ($\lambda = 632.8$ nm) at 25°C. Poly 1a ($dn/dc = 0.0929$ ml/g); poly 1b ($dn/dc = 0.0819$ ml/g); poly 1c ($dn/dc = 0.0662$ ml/g).

Glass transition temperatures were determined by DSC (PL Thermal laboratories) after extrapolation to zero heating rate.

The $^1\text{H-NMR}$ spectroscopic data of the homopolymers are reported in the literature (7) and the results of quaternized homopolymers are as follows:

Poly[5-(N,N,N-trimethylammonium)isoprene] -2a: $^1\text{H-NMR}$ (D_2O , 200 MHz): $\delta = 5.93$ (s br., 1H, $\text{HC}=\text{C}$), 3.87 (s br., 2H, $\text{C-CH}_2\text{-N}^+$), 3.00 (s br., 9H, $\text{R-N}^+(\text{CH}_3)_3$), 2.21 (s br., 4H, CH_2 -allyl). $^{13}\text{C-NMR}$ (D_2O , 50 MHz): $\delta = 140.85$ (C-2), 127.3 (C-3), 64.7 (C-5), 55.3 ($\text{N}^+(\text{CH}_3)_3$), 36.6 (C-1), 29.4 (C-4).

Poly[5-(N,N-diethyl-N-methylammonium)isoprene] -2b: $^1\text{H-NMR}$ (D_2O , 200 MHz): $\delta = 5.91$, 5.73 (s br., 1H, $\text{HC}=\text{C}$), 3.70 (s br., 2H, $\text{CH}_2\text{-N}^+$), 3.11 (q br., 4H, $J = 7$ Hz, $\text{-N}^+(\text{CH}_2\text{CH}_3)_2$), 2.83 (s br., 3H, $\text{R}_3\text{N}^+\text{CH}_3$), 2.20 (s br., 4H, CH_2 -allyl), 1.20 (t, $J = 7$ Hz, 6H, $\text{-N}^+(\text{CH}_2\text{CH}_3)_2$).

Poly[5-(N,N-dipropyl-N-methylammonium)isoprene] -2c: $^1\text{H-NMR}$ (D_2O , 200 MHz): $\delta = 5.95$, 5.72 (s br., 1H, $\text{HC}=\text{C}$), 3.68 (s br., 2H, $\text{CH}_2\text{-N}^+$), 3.22 (s br., 3H, $\text{R}_3\text{N}^+\text{CH}_3$), 2.97 (m br., 4H, $J = 7.5$ Hz, $\text{N}^+(\text{CH}_2\text{CH}_2\text{CH}_3)_2$), 2.17 (s br., 4H, CH_2 -allyl), 1.65 (m br., 4H, $\text{-N}^+(\text{CH}_2\text{CH}_2\text{CH}_3)_2$), 0.88 (t, $J = 7$ Hz, 6H, $\text{-N}^+(\text{CH}_2\text{CH}_2\text{CH}_3)_2$).

Poly[5-(N,N-diisopropyl-N-methylammonium)isoprene] -2d: $^1\text{H-NMR}$ (D_2O , 200 MHz): $\delta = 5.62$ (s br., 1H, $\text{HC}=\text{C}$), 3.60 (s br., 7H, $\text{-N}^+(\text{CH}(\text{CH}_3)_2)_2$, $\text{C-CH}_2\text{-N}^+$, $\text{R}_3\text{N}^+\text{CH}_3$), 2.18 (s br., 4H, CH_2 -allyl), 1.15 (d, 12H, $\text{-N}^+(\text{CH}(\text{CH}_3)_2)_2$).

Results and discussion

Homopolymerization

Preliminary experiments on the anionic homopolymerization of aminoisoprenes in cyclohexane, benzene or hexane at different temperatures showed that monomer conversion was lower than 30% and decreases with increasing temperature.(6) Based on these results the aminoisoprene polymerization was carried out in toluene at -40°C , using *sec*-butyllithium as initiator. Under these conditions a quantitative conversion of 5-(*N,N*-dialkylamino)isoprene should be reached as reported in a recent work. (11) Table 1 shows the characterization of the homopolymers used in this study. The polymer microstructure was determined as described elsewhere.(7)

Table 1 – Characterization of unquaternized homopolymers

Polymer	Microstructure			M_w^b	M_w^c	M_w/M_n^c	Yield ^{d)}	T_g^e
	4,1-cis	4,1-trans	4,3-units	(g/mol)	(g/mol)		%	($^{\circ}\text{C}$)
1a	9	91	--	38000	--	--	52	-39
1b	13	86	<1	33400	39800	1.3	60	-47
1c	6	93	<1	54300	61400	1.5	25	-56
1d ^{a)}	>95	--	<5	--	24000	1.4	50	-11

a) polymerized in *n*-hexane at -40°C .

b) from static light scattering measurements.

c) from size exclusion chromatography using polystyrene standards.

d) determined by gravimetry .

e) obtained by extrapolation to zero heating rate.

The polymer microstructure and the glass transition temperature strongly depend on the bulkiness of the alkyl substituent attached to the amino group. While polymers with linear alkyl substituents (methyl, 1a; ethyl, 1b; propyl, 1c) have high contents of 4,1-trans units, polymer 1d has a high content of 4,1-cis units. This differing microstructure is mainly due to the bulkiness of the diisopropyl group, which favors a *s-cis* geometry of the monomer and hinders the cis-trans isomerization at the end of the living chain which shows a 4,1-*s-cis* structure in non-polar solvents.(12) The complexation of the Li^{\oplus} counter ion at the end of the carbanionic chain with the amino group of the incoming monomer also contributed to this stereoselectivity. The formation of these complexes was confirmed by NMR studies of the living carbanionic species (12) and by kinetic experiments.(9) In the case of polymers 1a-c the steric requirement of the side groups is not large to inhibit the isomerization at the end of the chain and a polymer with high contents of 4,1-trans units is formed. The observed microstructure of polymer 1b is quite different from that reported

earlier (7), in which a polymer ($M_n = 8000$ g/mol) with almost equal amounts of 4,1-cis and 4,1-trans units was obtained. This indicates that the polymer microstructure of poly-aminoisoprenes depends also on the monomer/initiator ratio as observed for the polyisoprene polymerization in cyclohexane (13). In other polymerizations of 5-(N,N-dipropylamino)isoprene in benzene, an increase of the 4,1-trans units with the polymer chain length was observed.(14) However, more studies are necessary to explain these results.

Despite the fact that the aminoisoprenes are monomers with a polarity similar to triethylamine, only small fractions of 4,3-units are incorporated to the polymer backbone. It demonstrates that the monomer addition to the end of the carbanionic chain occurs almost exclusively by 4,1-addition.

The non-quantitative monomer conversion has been explained by the formation of intramolecular complexes at the end of the living chain involving the amino groups located at the polymer backbone. Such complexation would hinder the addition of the monomer to the carbanion. However, the quantitative conversion obtained with 5-(N,N-dimethylamino)isoprene (11) reveals that the addition of the monomer to these associated species takes place and originates a broadened molecular weight distribution as observed here. The lower conversion obtained in this work could be related to the longer reaction times, since the polymerization typically is over after 15-30 min (11). Morschhäuser (14) found that waiting a longer times leads to a decrease of molecular weight. Nonetheless the influence of the alkyl substituent and the presence of some impurities may not be disregarded to explain the limited yield.

The ponderal average molecular weights obtained through SEC are higher than those from SLS measurements. Polymer 1a could not be characterized by SEC using standard crosslinked polystyrene columns. The high basicity of this tertiary amine causes complete adsorption of the polymer on the column material. (11) For other polymers monomodal SEC traces with a tailing to higher elution volume probably due to absorption processes are obtained.

The glass transition temperature T_g , as expected, decreases with increasing the alkyl substituent length but it is higher for polymer 1d which has bulky diisopropyl substituents. Polymers 1a and 1d are semi-crystalline and show, at first heating in DSC measurements, a broad melting interval around 60°C and 75°C, respectively. This transition was not observed for polymers 1b and 1c.

Quaternization

The quaternization of the polymer takes place easily due to the high basicity of the tertiary aliphatic amine in comparison to the aromatic amino group of polyvinylpyridine or polyaniline. The reaction was performed at room temperature in a mixture of solvents

(methanol/benzene) and dimethyl sulfate. Methyl iodide and benzylic chloride could also be used as alkylation reagents, however in this case the reaction is not quantitative and moreover the polymer degrades. The quaternized polymer is soluble in water, as a cationic polyelectrolyte, and the completion of the reaction is shown by $^1\text{H-NMR}$ spectroscopy.

Figure 1 shows the $^1\text{H-NMR}$ spectrum for the unquaternized and quaternized poly[5-(N,N-dimethylamino)isoprene]. The resonance signals of the allylic protons of the polymer backbone for unquaternized polymer and the methyl protons of the alkyl substituent of the amino group are overlapping at 2.2 ppm. The resonance peak at 5.3 ppm is characteristic of the vinylic proton of 4,1-units, whereas the signals of 4,3 units are absent. The assignment of the polymer microstructure (cis- and trans-4,1-units) is performed by the signals around 3.0 ppm, which arise from the methylene protons attached to the carbon C-5. (7)

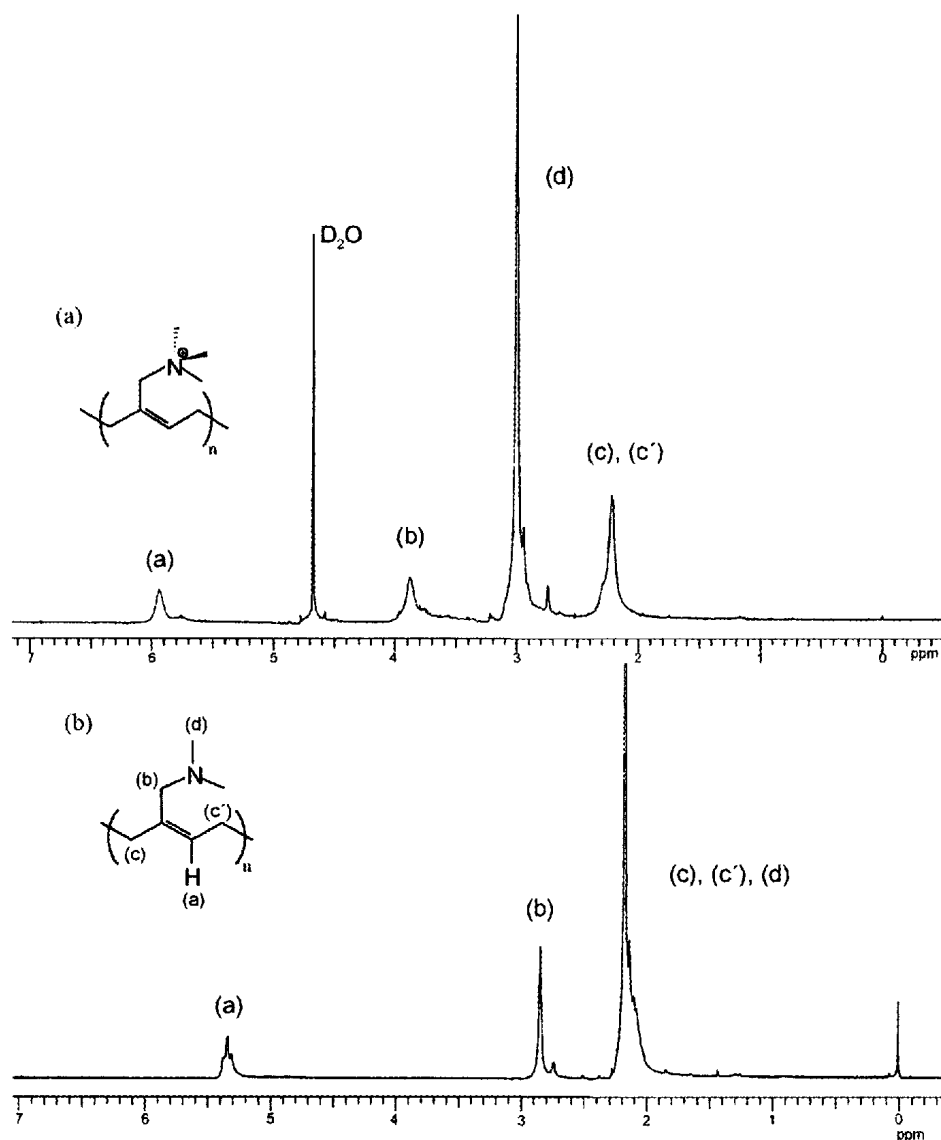


Figure 1 – $^1\text{H-NMR}$ spectra of quaternized and unquaternized poly[5-(N,N-dimethylamino)isoprene]. (200 MHz, (a) D_2O , (b) CDCl_3)

According to the literature (7) the signal at 2.85 ppm corresponds to the trans isomer and the signal at 2.71 ppm to the cis 4,1-unit. Through quaternization these resonance signals are broader and shifted to lower field (3.87 ppm) due to the positive charge on the nitrogen atom. The vinyl and methyl protons are also observed at lower field, respectively, around 5.9 and 3.0 ppm. However, the position of the signal for the allylic protons remains practically unchanged (2.2 ppm). All quaternized polymers show similar behavior and the proton assignment is described in the experimental section.

In the ^{13}C -NMR spectrum (200MHz, D_2O) of the quaternized poly[5-(N,N-dimethylamino)isoprene] a resonance shift to lower field is observed for all carbon signals especially for carbon atom C-5, where the signals can be observed at 58.4 ppm in the ^{13}C -NMR spectrum of the unquaternized polymer and at 64.7 ppm in the ^{13}C -NMR spectrum of the quaternized polymer. The methyl groups linked to the positively charged nitrogen atom shift from 45.4 to 55.3 ppm.

Phase transfer polymerization

Quaternized poly[5-(N,N-diisopropylamino)isoprene] was used as phase transfer catalyst for the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide), PPO, from 4-bromo-2,6-dimethylphenol (BDMP). The polymerization in a two-phase system (toluene/aqueous NaOH), in presence of air, at room temperature takes place through a single electron transfer mechanism (15). Thus, polymers with number average molecular weight up to 50.000 g/mol can be obtained. This was not possible by the oxidative coupling polymerization of 2,6-dimethylphenol with copper complexes.(16). This reaction was performed as described by Percec (15), using quaternized polymer as phase transfer catalyst instead of tetrabutylammonium hydrogensulfate (TBAH). After 12 hours, the reaction was quenched with concentrated HCl. The polymer was precipitated in methanol and then dried under vacuum to be characterized by ^1H -NMR and SEC.

The ^1H -NMR-spectrum shows the characteristic singlet signals from the aromatic and methyl protons at 6.5 and 2.0 ppm, respectively. The conversion was about 50% and a polymer with a higher molecular weight ($M_n = 75000$ g/mol) and narrower molecular weight distribution ($M_w/M_n = 1,9$) than the synthesized polymers with TBAH was obtained.

This result is very encouraging for using this quaternized polymer as phase transfer catalyst. Additional examples of phase transfer catalyzed reactions have also been performed in our laboratory and the solution properties of the cationic polyelectrolytes are under investigation.

Acknowledgements

This work has been supported by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico do Brasil), FAPERGS (Fundação do Estado do Rio Grande do Sul) and CAPES/PROBRAL program.

References

1. Tomalia DA. (1989) In: Kricheldorf, H.R. (ed) Handbook of Polymer Synthesis. Part A. Marcel Dekker Inc. London
2. Goethals EJ. (1979) Polymeric Amines and Ammonium Salts, Pergamon Press. Oxford
3. Hoover MF. (1970) J.Macromol. Sci.-Chem. A4(6):1327
4. Vorchheimer N. (1988) In: Encyclopedia of Polymer Science Wiley & Sons New York (vol. 11, pp 489)
5. Hogen-Esch TE, Tien CF. (1980) Macromolecules 13:207
6. Petzhold C, Stadler R, Frauenrath H. (1993) Makromol. Chem., Rapid Commun. 14:33
7. Petzhold C, Morschhäuser R, Kolshorn H, Stadler R. (1994) Macromolecules 27:3707
8. Petzhold C. (1994) PhD Thesis. Universität Mainz - Germany.
9. Mannebach G, Morschhäuser R, Stadler R, Petzhold C. (1998) Macromol. Chem. Phys. 199: 909
10. Bruice TC, Kharasch N, Wizzler RJ. (1953) J. Org. Chem. 18:83
11. Bieringer R, Abetz V. submitted to Polymer
12. Petzhold C, Kolshorn H, Stadler R. (1995) Macromol. Chem. Phys. 196: 1405
13. Worsfold DJ, Bywater S. (1978) Macromolecules 11:582
14. Morschhäuser R. (1997) PhD Thesis. Universität Mainz - Germany.
15. Percec V, Shaffer TD. (1986) J. Polym. Sci., Polym. Letters 24:439
16. Challa G, Chen W, Reedijk J. (1992) J.Macromol. Chem , Macromol. Symp. 59, 59