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Polyelectrolytes

2. A New Cyclic Quaternary Ammonium Polymer Poly(N,N-Dimethyl-3,4-Pyrrolidinium) Bromide

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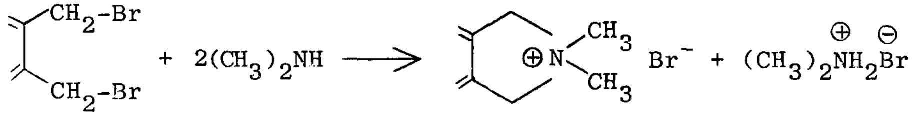
SUMMARY

The polymerization of N,N-dimethyl-3,4-dimethylene-pyrrolidinium bromide was carried both in the presence and absence of initiators. Aqueous solutions with 10-50% monomer were polymerized by heating at 60°. The conversion time decreased with increased monomer concentration and molecular weight increased with increased monomer concentration. High monomer concentration also yielded significant amounts of monomer dimer.

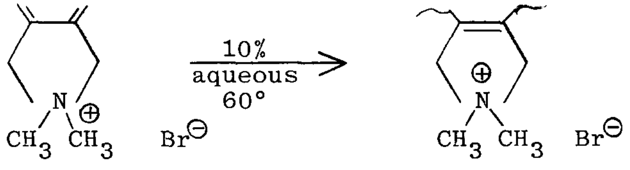
In an earlier report, we described the formation of polyelectrolytes by reacting 2,3-bis(bromomethyl)-1,3-butadiene I with various ditertiary amines (1).

As part of our study involving the synthesis of polyelectrolytes, we have prepared a new cyclic quaternary ammonium monomer N,N-dimethyl-3,4-dimethylene-pyrrolidinium bromide (II) by reacting dimethylamine with 2,3-bis(bromomethyl)-1,3-butadiene (I).



I II

Aqueous solutions of II were readily polymerized at 60°. The NMR spectrum of the polymer is consistent with 1,4-polymerization of the diene system to give poly(N,N-dimethyl-3,4-



II III

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dimethylenepyrrolidinium) bromide III. When the monomer concentrations were greater than 10%, polymerization occurred in aqueous solution without initiator. The spontaneous polymerization in aqueous solution of quaternary ammonium systems is not unique and has been reported by Salomone (2). Various initiators were used with varying results. For example, 1% t-butyl hydroperoxide yielded 100% conversion in 5 hrs with 20% monomer concentration whereas the corresponding noncatalized system yielded 93% conversion after 24 hrs and ammonium persulfate, on the other hand, produced 77% conversion after 24 hrs. The latter inhibition may be caused by bromide ion oxidation by the persulfate to generate bromine which would act as an inhibitor (3).

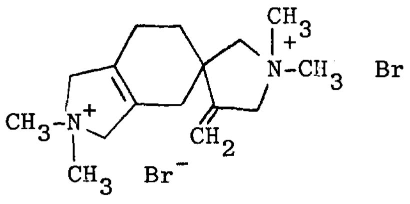
In an attempt to form a polymer with a high molecular weight, the effect of varying the concentration of the monomer on the molecular weight was studied. The results are shown in Table I.

TABLE I. Effect of Monomer Concentration on Polymerization

Na	Monomer Concentration%	Temperature °C	Time hr	Yield	Intrinsic Viscosity (dl/g)[a] Of Polymer	Polymer Extracted with Methanol
1	10	60	24	45	1.35	2.55
2	20	60	24	81	1.75	2.72
3	40	60	5	100[b]	3.90	6.4
4	50	60	5	100[b]	4.05	8.5
5	60	60	5	100[b]	Gel	Gel

a) Measured in 2.0M KBr at 30°C.
b) Contains 5-10% of a dimer formed by a self Diels-Alder Reaction

The polymerizations were carried out in water solution and precipitated by adding the polymer solution to acetone. The intrinsic viscosity of the precipitated polymer was determined before and after the polymer had been soaked in methanol. Analysis of the polymerization mixture indicates that at low monomer concentrations, 10-20%, the mixture contains unreacted monomer and polymer. At high concentrations, 40% and higher, the mixture contains a significant amount (5-10%) of a dimer IV which is formed by a self Diels-Alder reaction of the monomer. After precipitation of the polymer, it was found that unreacted monomer and the dimer could be readily extracted by titurating with methanol.



IV

The results in Table I also indicate that even at low monomer concentrations (10-20%), a low molecular weight polymer ($[\eta]$ = 1.3-1.7 dl/g) is formed. At high monomer concentrations (40-50%) viscosity measurements ($[\eta]$ = 6.4-8.5 dl/g) indicate the formation of a very high molecular weight polymer. When the monomer concentration was increased in excess of 50% and intractable gel is formed indicating that some crosslinking may be occurring.

EXPERIMENTAL

N,N-Dimethyl-3,4-dimethylenepyrrolidinium Bromide

A solution of 12 g (0.05 mol) of 2,3-bis(bromomethyl)-1,3-butadiene (4) in 60 ml of methanol was added dropwise with stirring to a solution of 4.5 g (0.10 mol) of dimethylamine in 50 ml of methanol cooled in an ice bath. After the addition was complete, stirring at room temperature was continued for one hour, then 3.3 g (0.05 mol) of 85% KOH pellets were added and stirring continued until all the KOH dissolved. After standing a short time, the precipitated KBr was removed by filtration. The filterate was concentrated by rotatory evaporation and the product precipitated by the addition of 1:1 acetone-ether mixture. The precipitate was filtered, washed with ether, vacuum dried, recrystallized from acetonitrile-ether and again vacuum dried to yield 8.0 g (77%) of N,N-dimethyl-3,4-dimethylenepyrrolidinium bromide; mp > 300°C; NMR (D_2O) δ 5.77 (m, 2H, $H_2C^=$) 5.30 (m, 2H, $H_2C^=$), 4.28 (m, H_2C^-), and 3.17 (s, 6H, CH_3-N); IR (KBr) 3080, 3005, 1630, 1460, 1445, 1440, 1345, 1295, 1220, 990 and 915 cm^{-1}.

Anal. Calcd for $C_8H_{14}NBr$: C, 47.07; H, 6.91; N, 6.86. Found: C, 46.99; H, 6.82; N, 6.88.

Polymerization

A solution of 0.50 g of monomer in 2.0 ml of distilled water was made up in a pyrex tube which was then put through three freeze thaw cycles under vacuum and sealed. The tube was then heated in a 60° oil bath for 24 hours. The solution was added to 50 ml of acetone and the precipitated material filtered,washed with acetone and vacuum dried to give 0.41 g, (82%) of polymer. NMR (D_2O) δ 4.35 (s, 4H, H_2C-N), 3.27 (s, 6H, H_3C-N), and 2.33 (s, 4H, H_2C^-) ppm. The intrinsic viscosity in 2.0 M KBr at 30°C, determined using a Cannon-Ubbelohde semi-micro dilution viscometer, was 1.70 dl/g.

Polymerization and Isolation of Dimer

A solution of 1.0 g of monomer in 1.0 ml of distilled water was sealed in a pyrex tube as described above. After heating in a 60° oil bath for 5 hours, the tube was opened and the contents transfered to 50 ml of acetone which precipitated the polymer. The precipitate was collected by filtration and vacuum dried to yield 1.09 g of material. The intrinsic viscosity of this material in 2.0 M KBr at 30°C was 4.0 dl/g. The polymer was then soaked in methanol until it was soft enough to cut into thin strips. The polymer strips were left soaking in methanol for 48 hours, collected by filtration and vacuum dried. About 15% of the product dissolved in methanol. The dissolved material was shown to consist of retained water, unreacted monomer and a self Diels-Alder adduct of the monomer. The extracted polymer had an intrinsic viscosity of 7.0 dl/g, measured in 2.0 M KBr at 30°C. The methanol solution was evaporated to dryness and the residue vacuum dried to leave 90 mg of impure dimer (IV). Recrystallization from acetonitrile gave 20 mg of pure dimer IV. NMR (D_2O) δ 5.5-5.4 (m, 2H, H_2C) 4.36 (m, 6H, $CH_2-\overset{+}{N}$), 3.70 (s, 2H, $H_2C-\overset{+}{N}$), 3.3-3.2 (m, 12H, CH_3-N), 2.5-1.8 (m, 6H, H_2C^-). All polymers obtained was treated in a similar manner to remove the dimeric material.

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