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Cyclopolymerization. X. Salt Retention by Ordered and Disordered Amphoteric Copolymers

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ABSTRACT

A study of the copolymerization of certain weak acid and weak base monomers has been undertaken in order to ascertain the conditions yielding products suitable as desalination resins. Salt retention by copolymers of methacrylic acid and N,N-dimethylaminoethyl methacrylate was examined first. Copolymers formed with acid and base groups arranged alternately along the polymer chain do not retain salt, whereas copolymers having a random arrangement of acid and base groups retain salt strongly. Attempts to prepare copolymers, suitable for desalination, from allylamine and methacrylic acid monomers has so far failed. The resulting products are generally poly(methacrylic acid), with amine or amine homopolymer bound to the polyacid chain. True copolymers, although present, are less prevalent. The implication of these results to copolymerization, in general is discussed.

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INTRODUCTION

Synthetic polymers which contain both acidic and basic groups have been studied in the past largely because of their relation to many of the naturally occurring biologically important polymers. These synthetic materials are now important in a number of commercially significantly areas, for example in ultrafiltration and dialysis membranes [1], in water demineralization processes [2], and in medical applications [1].

Recently, thermally regenerable resins made from mixtures of weakly acidic and weakly basic polymers have been proposed for use in the desalination of brackish water [3, 4]. Copolymers of carboxylic acids and amines, rather than homopolymer mixtures, might have a greater desalination efficiency, because the proximity of the acid and base sites may enhance the rate of salt adsorption. However, experimentally produced materials had a greatly reduced salt uptake capacity unless special precautions are taken to minimize the tendency of the acid and base units to neutralize each other [5, 6].

A major problem, always present in copolymerization work is how to establish the detailed structure of the product. This problem is accentuated where strongly interacting monomers such as acids and bases are used. Then the possibility of intertwined homopolymer mixtures is particularly difficult to eliminate. With diallylamine polymers the degree of structural uncertainty is compounded because the materials are often crosslinked and the two allyl groups can either react as chain transfer agents or propagate in a cyclized or uncyclized form. Although there have been a number of reports of diallylamine amphoteric copolymers in the literature [7], structural evidence for the formation of true copolymers is generally lacking [8, 9].

The objective of this paper is twofold: first, to relate internal acid-base self-neutralization with efficiency of salt-retention for several well-established copolymers, and second, to determine the structures of the amphoteric polymers produced when mixtures of allylamino and acid monomers are polymerized.

COPOLYMERS OF METHACRYLIC ACID AND DIMETHYLAMINOETHYL METHACRYLATE

In order to see if internal neutralization in an amphoteric copolymer reduces salt uptake, we chose as our model copolymers those from methacrylic acid and N,N-dimethylaminoethyl methacrylate, the diethylamino analogs of which have been characterized by Alfrey, Overberger, and Pinner [10]. It should be noted that these workers

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did not produce direct evidence of copolymer structure; instead this was deduced mainly from comparison of acid/base ratios in the products and initial monomer mixtures. The copolymers were believed to have a random sequence of their acid and base units if prepared at pH 1.2 but an alternating sequence if prepared at pH 7.2. One would expect the copolymer prepared at pH 7.2 to have the maximum possible extent of self neutralization whereas the copolymer prepared at pH 1.2 should have some unreacted groups. Calculations using various models of the copolymer containing equal numbers of acid and base sites indicate that between one quarter and one third of the acid (base) sites will be neutralized by adjacent base (acid) sites.

Aqueous solutions of the two types of polymers together with excess sodium chloride were placed in cellulose dialysis bags and dialyzed by using stirred, distilled water. At regular intervals the sodium content of the salt ions in the dialysis bags was determined by atomic absorption spectroscopy. The results are shown in Table 1.

Our results show that the random copolymer (pH 1.2) and poly(methacrylic acid) retain salt quite strongly, whereas the alternating copolymer and poly(N,N-dimethylaminoethyl methacrylate) do not.

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TABLE 1. Total Sodium in Solutions after Various Times of Dialysis[a]

	Total Na (mg)			
Polymer	0 hr	4 hr	22 hr	46 hr
Poly(methacrylic acid)	37.0	2.1	1.5	0.9 (0.8)[b]
Poly(N,N-dimethylaminoethyl methacrylate)	37.0	0.7	0.1	0.1
Copolymer (pH 1.2)[c]	37.0	4.8	2.7	2.4 (1.6)[b]
Copolymer (pH 7.2)[c]	37.0	0.8	0.1	0.0

[a] The solutions initially contained 200 mg of polymer dissolved in 30 ml water; reaction temperature 25.0 ± 0.1°C. Allowance was made for the loss of solution in sampling and for the variation of volume during dialysis.

[b] Approximate chlorine content (mg) as determined by elemental analysis.

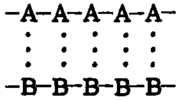
[c] The copolymer (pH 1.2) contained 5.16% N and the copolymer (pH 7.2) contained 5.22% N. Expected for 0.5 mole fraction of amine in polymer: 5.75% N.

These results can be rationalized by assuming that the acid sites of the alternating copolymer (pH 7.2) are neutralized by the adjacent base sites, making this copolymer incapable of retaining salt. The random copolymer will not have all its sites intramolecularly neutralized. Therefore our results not only indicate that certain copolymers can act as desalinating agents but also give chemical verification for the structures proposed by Alfrey et al. for the diethylamino analogs.

In our work we have also tried to get more direct evidence of the structure of these polymers. Firstly we attempted to establish by further chemical means that the copolymer (pH 7.2) was indeed true copolymer (such as I) rather than intimately bound homopolymer mixture (such as II). A preprepared mixture of homopolymers

$$-A-B-A-B-A-B-$$

I



$$\begin{array}{c}-A-A-A-A-A-\\ \vdots\ \ \vdots\ \ \vdots\ \ \vdots\ \ \vdots\\ -B-B-B-B-B-\end{array}$$

II

where

A = $CH_2CH(CH_3)CO_2H$

B = $CH_2C(CH_3)CO_2CH_2CH_2N(CH_3)_2$

differed from copolymer (pH 7.2) in being insoluble in water. Excess hydrochloric acid was added to solutions of both copolymer (pH 7.2) and the homopolymer mixture. The polymer remained soluble and the homopolymer mixture dissolved. After 3 hr an equivalent of sodium hydroxide (to hydrochloric acid) was added to both solutions. The homopolymer mixture precipitated but the copolymer remained soluble. If the copolymer had been a homopolymer mixture with a structure such as II, then we might have expected that hydrochloric acid would break it apart to separated homopolymers. This would result in polymer precipitation after addition of sodium hydroxide, exactly as found for the homopolymer mixture. The fact that a precipitate did not form is supporting evidence that copolymer (pH 7.2) is, indeed, a polymer. Further evidence for this conclusion was that the sodium chloride in the final solution of copolymer II could be readily removed by dialysis. If a mixture of homopolymers had been present, the salt would probably have been retained because poly(methacrylic acid) retains salt quite strongly (Table 1).

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Recently, ^{13}C NMR has been developed into a very powerful technique for structural studies in polymers and appears to be a particularly appropriate one in this case. Details of the methods used and the type of instrument have appeared in previous papers [11, 12] and will not be repeated here. Spectra of a number of different samples of the two homopolymers and the two copolymers were determined in both water and salt solution and the results compared. This technique enabled us to distinguish between the various types of polymers. Examples are shown in Fig. 1. The most noticeable feature of the spectra was the high resolution of the alternating copolymer when compared to the random copolymer. The tetrasubstituted carbon atoms at 44 and 46 ppm are especially noticeable and would probably be so sharp only for an ordered structure with little conformational variation. With the random copolymer, all peaks except the N-methyls were broad, as expected for a structure with many different conformational variations.

The second feature of the spectra was the shift of 3 ppm for the backbone methylene carbon positions from the homopolymer to the alternating copolymer. Because these positions are the furthest from the basic nitrogen atom but are shifted the most, the copolymer is unlikely to be just an acid/base association of the homopolymers, as seen in structure II. Detailed analysis of each individual peak in all the spectra was not possible because the resolution was not sufficient to separate all the various conformational isomers.

Our results thus show that the acid-base sequence in the copolymer can be important in determining the efficiency of salt retention. They suggest that internal neutralization decreases the efficiency enormously. A random copolymer containing an equal number of acid and base groups will have a relatively small fraction of its sites not internally neutralized, but the results imply that these nonneutralized sites are highly efficient.

COPOLYMERIZATION OF DIALLYLAMINO MONOMERS WITH ACRYLIC ACIDS

The second section of our work was concerned mainly with the copolymerization of various diallylamino monomers with methacrylic or acrylic acid. As the amine and acid are two very different types of monomer with an expected large difference in reactivity ratios, one would anticipate some copolymerization problems [8]. Most of the previously described copolymerization experiments [13-15] indicate that the resulting polymers contained amine (although never more than about 30 mole%) but, except for the work of Jones with allylamine [8], no real effort was made to determine the copolymer structure.

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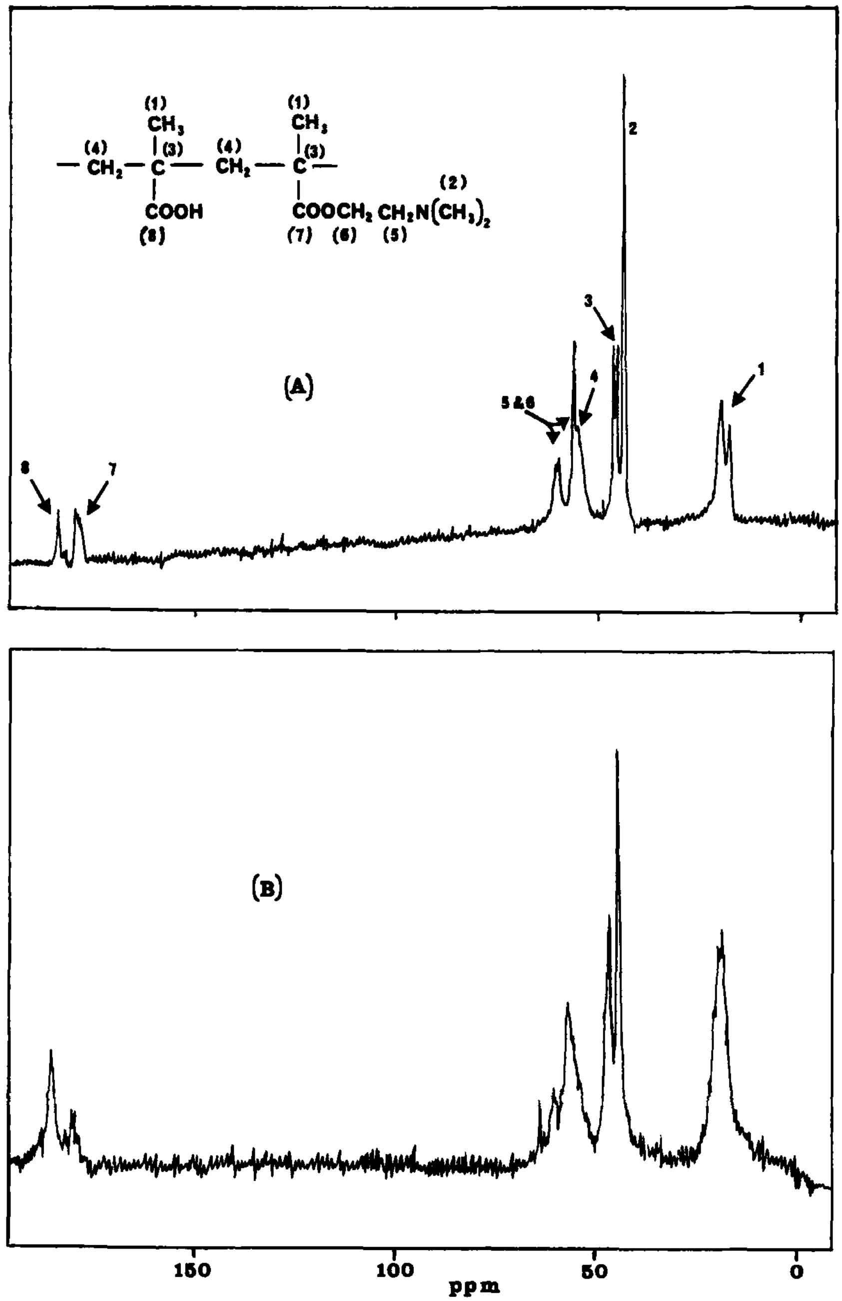

FIG. 1. Proton-decoupled natural abundance ^{13}C NMR spectra of (A) alternating and (B) random copolymers of N,N-dimethylaminoethyl methacrylate and methacrylic acid.

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In our initial work, readily available diallylamine derivatives such as N-methyldiallylamine and triallylamine were polymerized in aqueous solutions or organic solvents with many different types of initiators. In general the mole ratio of amine to acid in the resulting "copolymers" was about 1:3 at most initial monomer ratios. Surprisingly, this did not vary significantly with changes of pH from 7 to 1 or with monomer ratios from 1:3 to 3:1. These results were comparable to the ratio of 1:4 obtained by the Russian workers Shcherbina and Fedorova [15]. The polymers produced were extensively washed with solvents, and in most cases mild acid or alkali washes were also used to try to remove any additional strongly bonded monomer or homopolymer.

Use of crosslinkable amino monomers such as triallylamine caused the formation of crosslinked copolymers while simple diallylamine monomers gave soluble polymers, as is consistent with cyclocopolymerization. However, proton magnetic resonance and infrared spectra of these materials indicated that a considerable proportion of the allylic groupings in the molecule had not reacted; even with alkyl-substituted diallylamines.

Because of the ambiguous physical evidence more detailed studies of this type of copolymer were carried out. A series of substituted diallylamino monomers was copolymerized with methacrylic acid under controlled conditions. The amine monomers included a number of new compounds (Table 2) recently synthesized and homopolymerized [16]. To avoid problems encountered in the isolation of these amphoteric polymers from aqueous solutions, the polymers were synthesized in organic solvents with azobisisobutyronitrile initiator. As inorganic ions were not used a slight excess of an organic acid was present in all experiments. This was generally methacrylic acid.

Table 2 gives a list of the "copolymers" produced and their properties. All the polymers were extracted exhaustively with various organic solvents ranging in polarity from benzene to ethanol to remove unchanged monomers. Samples of each polymer were also treated with dilute (0.1 N) hydrochloric acid and sodium hydroxide and extracted with ether to see if any unchanged monomer was loosely bound to the polymer. In most cases no significant quantity was extracted.

Proton magnetic resonance spectra of the soluble polymers (in DMSO-d_6) still indicated that a high proportion of allyl groupings remained within the "copolymer;" even at 100 Hz the resolution of the peaks was insufficient to determine the detailed structure. The possible structures of these "copolymers" include the following: (a) poly(methacrylic acid) plus tightly bound monomer; (b) poly(methacrylic acid) plus intertwined homopolymeric aminopolymer;

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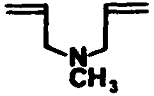
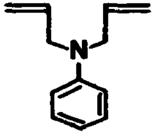
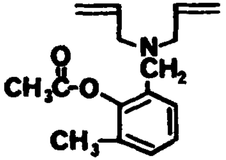
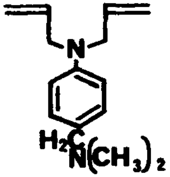
TABLE 2. "Copolymerization" of Methacrylic Acid and Diallylamino Monomers

No.	Amino monomer structure	Amine (mole %) In monomer mixture	Amine (mole %) In polymer[a]	Yield (%)	Limiting viscosity (dl/g)[b]	Polymer properties[c]
III		50	25	42	0.35	Colorless, soluble in base insoluble in acid
IV		50	33	39	0.25	Colorless, soluble in strong base and acid
V		50	22	32	0.22	Colorless, soluble in strong base and acid, also between pH 7 and 6.
		33	17	61	0.26	
		66	27	18	0.15	Light brown
VI		50	28	36	0.06	Slightly brown, soluble in strong base and acid, also between pH 10 and 6

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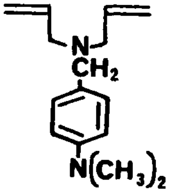
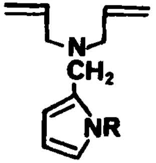
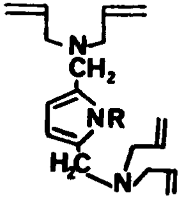
VII			50	20	34	0.12	Slightly brown, soluble in strong base and acid also between pH 8 and 6
			33	14	29		
			66	30	22		Dark brown and sticky
VIII		R = H	50	17	32	0.09	Brown, decomposed readily
IX		= CH_3	50	18	60	0.15	Colorless, soluble in strong base and acid
X		R = H	50	25	39	–	Light brown, insoluble, decomposed slowly
XI		= CH_3	50	26	43	–	Light brown, insoluble
			33	8			
			66	22	14		

---

[a] Calculated from the results of carbon, hydrogen, and nitrogen analysis.

[b] In dimethyl sulfoxide solution.

[c] On titration from strongly basic to acid solution the polymers often dissolved and reprecipitated a number of times as noted.

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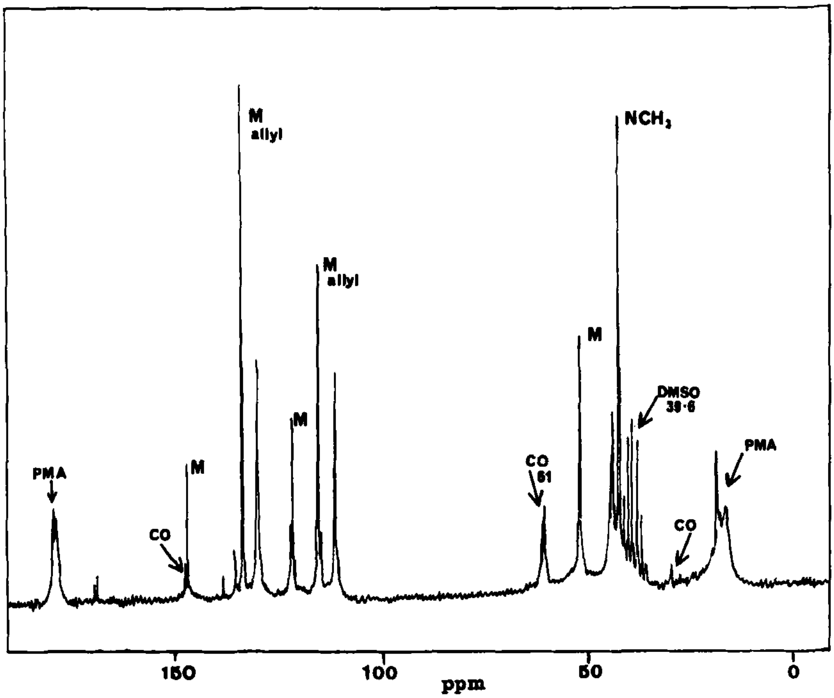

FIG. 2. Proton-decoupled natural abundance ^{13}C NMR spectra of "copolymer" of 1-diallylamino-4-dimethylaminomethylbenzene (VI) and methacrylic acid. CO denotes cyclic copolymer; M denotes monomer; PMA is poly(methacrylic acid).

(c) poly(methacrylic acid) chain terminated with amino monomer units; (d) true copolymer with cyclopolymerization of amino monomer; (e) true copolymer with one allyl group reacted; (f) combinations of the above.

Detailed ^{13}C NMR spectroscopy coupled with some of the physical properties was able to distinguish between these structures. Using model compounds and the ^{13}C NMR spectra of the homopolymers [11, 12, 16], we were able to show that the bulk of the amino monomers incorporated in the copolymers were present only as tightly bound monomer. However, in most cases, some covalently bound amino monomer was also present to a certain extent, as evidenced by the polymer solubilities. For two of the copolymers (the structures with amines IV and VI) sufficient of the amino cyclocopolymerized with the methacrylic acid to be readily distinguished in the ^{13}C spectra (Fig. 2).

TABLE 3.

Amine monomer	Amine in "copolymer" (mole %)	Amine covalently bonded (%)[a]
III	25	$\simeq$0
IV	33	$\simeq$70
V	22	<10
VI	28	$\simeq$30
VII	34	$\simeq$15
IX$_{R=CH_3}$	18	<10

[a] Determined by ^{13}C NMR and drastic extraction procedures; results are accurate only to ± 5%.

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The most easily distinguished peak was the methylene adjacent to the nitrogen atom in the pyrrolidine nucleus (at about 60 ppm). The shifts in peak positions compared to those in the homopolymers showed that these species were truly cyclocopolymerized. Table 3 gives the maximum extent of the cyclocopolymerization of the various copolymers. Below 10% cyclocopolymerization of the amino monomer the use of ^{13}C NMR is impractical for an accurate assessment of the structure, but even at this value the viscosities of the polymers would indicate that the amino groups are more than just terminating groups on poly(methacrylic acid).

Because of the results obtained by ^{13}C NMR, more vigorous efforts were made to remove the amine monomers from the copolymers. For the "copolymer" from amine III a considerable portion of the amine could be removed by prolonged heating at very low pressures or repeated washing with acetic acid solution. For most of the other "copolymers" treatment with concentrated sodium hydroxide solution and continuous extraction with ether did slowly remove some of the amine monomer. This was generally accompanied by degradation of the "copolymer."

EXPERIMENTAL

Methacrylic acid was distilled from copper powder (bp 57° C/10 Torr; lit. bp 60° C/12 Torr) and stored at 0° C. N,N-Dimethylaminoethyl methacrylate was distilled (bp 30° C/0.1 Torr) immediately before use. All polymerizations were carried out under a nitrogen atmosphere.

^{13}C spectra were recorded on a Varian CFT-20 NMR spectrometer. IR spectra were measured by using a Perkin-Elmer 577 grating spectrophotometer. Sodium analyses were obtained by using a Varian-Techtron AA-5 atomic absorption spectrophotometer. Measurements of pH were made with a Pye model 291 pH meter.

Preparation of Polymers

The copolymers were prepared according to the method of Alfrey et al.

N,N-Dimethylaminoethyl methacrylate (15 g, 96 mmole) and methacrylic acid 10 g, 116 mmole) were dissolved in oxygen-free distilled water (180 ml) and the solution adjusted to pH 7.2 by using sodium hydroxide. Polymerization was initiated at ambient temperature by addition of potassium persulfate (0.1 g). After ca. 4 hr the viscous solution was poured into acetone (1.5 liters) and the resulting precipitate redissolved in water. Precipitation from acetone was repeated three times, and then the aqueous solution was dialyzed for 4 days. The product was dried, finally at 10^{-6} Torr and 70° C for 5 hr (yield 3.8 g). Analysis. Found: C, 57.4%; H, 9.1%; N, 6.2%; S, 0.3%; Na, 0.0 (by atomic absorption); Cl, 0.0 (by silver nitrate titration). Calculated for $C_{12}H_{21}NO_4$ (1:1 copolymer): C, 59.2%; H, 8.7%; N, 5.8%. Estimated mole fraction of amine in copolymer, 0.59. IR (KCl disk) 1725 cm^{-1} (C=O).

N,N-Dimethylaminoethyl methacrylate (15 g, 96 mmole) and methacrylic acid (10 g, 116 mmole) were dissolved in oxygen-free distilled water (180 ml) and the solution adjusted to pH 1.2 by using hydrochloric acid. Polymerization was initiated at room temperature by addition of potassium persulfate (0.1 g). After ca. 6 hr the product was precipitated twice from acetone; then the aqueous solution was adjusted to pH 8.0 using ammonium hydroxide. (Dialysis before neutralization did not remove all the chloride. Neutralization with sodium hydroxide gave a product which still contained large amounts of sodium after dialysis.) The product was precipitated two more times from acetone, then dialyzed for 4 days, dried, and heated to remove ammonia (10^{-6} Torr, 120° C, 4 hr). The resulting solid was redissolved in distilled water and again pumped dry (10^{-6} Torr, 120° C, 4 hr). The yield was 4.2 g. Analysis. Found: C, 56.1%; H, 7.5%; N, 5.2%; S, 0.0%; Cl, 0.0 (by silver nitrate titration). Calculated for $C_{12}H_{21}NO_4$ (1:1 copolymer): C, 59.2%; H, 8.7%; N, 5.8%. Estimated mole fraction of amine in copolymer, 0.46; expected from initial monomer ratio 0.45. IR (KCl disk) 1720 cm^{-1} (C=O).

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Sodium Retention Studies

The polymer (200 mg) was dissolved in distilled water (25 ml), then a solution (5 ml) of sodium chloride (95 mg) was added. A 1-ml sample was removed for initial sodium analysis; then the remaining solution was placed in cellulose dialysis tubing (1.59 cm diameter, 50 cm length). The tubing, tied at both ends, was immersed in a beaker of stirred distilled water (1800 ml), placed in a bath thermostatted at 25.0 ±0.1° C.

Samples for sodium analysis were removed by syringe at various time intervals (the dialysis tubing being retied below the syringe puncture). Changes in weight of the solution, due to osmosis and to sample removal, were monitored by weighing the solutions before and after each sample was taken. The distilled water was changed each time a sample was removed.

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Copolymerization of Diallylamino Monomers and Methacrylic Acid

The general method of polymerization was as follows. The two monomers (in 20 mmole quantities for 1:1 copolymerization) were dissolved in the organic solvent (50-70 ml of either benzene or tetrahydroform) in a two-necked flask with a nitrogen inlet and an outlet on a water-cooled reflux condenser. Azobisisobutyronitrile initiator (0.015 g) was then added, and the solution was irradiated overnight with a Philips 300-W high-pressure mercury ultraviolet lamp. The solution was magnetically stirred under a constant stream of dry nitrogen and kept at room temperature. The resulting polymer precipitate was then filtered and repeatedly washed with first benzene and then ether, tetrahydroform, chloroform, or ethanol. The final polymer was dried under reduced pressure (10^{-2} Torr) at 50-80° C for 48 hr.

Polymer formation was also initiated by thermal breakdown of the azobisisobutyronitrile but, in general, the polymers obtained were more highly colored (although they gave similar analytical results). Where higher than 50 mole % of amine monomer was used, excess acetic acid was added to the polymerization solution.

CONCLUSION

Weak acid/weak base copolymers have been shown to act as desalinating agents. The copolymer can not be of the alternating acid-base-acid . . . structure but needs to have acid and base groups which are not internally neutralized. Although the available groups on a polymer containing a random arrangement of acid and base groups act quite effectively, statistical calculations indicate that at least two thirds of the sites are internally neutralized. A polymer containing linked microblocks of acid and base groups should have most of its sites not neutralized and might provide the best compromise between the advantages of acid/base proximity and the disadvantages of internal neutralization [5, 6].

Copolymers of diallylamines and methacrylic acid have proved difficult to prepare, products being largely poly(methacrylic acid) with monomers or amine homopolymers associated along the chain. The difficulties are thought to be caused by the large difference in reactivities between the allylamine and methacrylic acid monomers [8].

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