Cyclopolymerization. XI. Polyelectrolytes and Polyampholytes from N-Alkyl-N, N-diallylamines and Methacrylamide

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ABSTRACT

The preparation and properties of some poly[$RN(CH_2CH=CH_2)_2$ hydrochlorides], where R may be methyl, n-propyl, n-hexyl, benzyl, and allyl, are discussed. Water-soluble polydiallyl-amine hydrochlorides have been prepared in high yields both by γ-irradiation and by chemical initiation. The polymers were characterized by solubility measurements, IR spectra, NMR spectra, and molecular weight determinations. Polydiallyl-amines as their free bases were found to gel both in solution and in the solid state; the factors influencing gelation were investigated. The polymerization of a mixture of methacryl-amide and either methyl- or n-propyldiallylamine hydrochlo-ride by chemical initiation and γ-irradiation in water, dioxane, and dimethylformamide was studied, and evidence is presented for and against the formation of a true copolymer. In all polymerizations, substantial quantities of either amine mono-mer or amine homopolymer were isolated. Although the amount of amine incorporated into the "copolymer" increased

959

with an increased amine:MAm ratio in the monomer feed, the
yield of "copolymer" decreased at a greater rate.

INTRODUCTION

Polyelectrolytes are used extensively as thickeners, dispersants,
water conditioners and in many paper, leather and textile applications
and, when crosslinked, as ion exchange resins [1, 2]. This paper
presents the preparation and properties of poly-N-alkyl-N, N-diallyl-
amines (RDAA) and the polyelectrolytes obtained by polymerizing a
mixture of an N-alkyl-N,N-diallylamine hydrochloride (RDAA·HCl)
and methacrylamide (MAm). MAm was chosen as the acid precursor
for several reasons. Firstly, attempts to copolymerize allylamine
and methacrylic acid have been unsuccessful with the homopolymer,
allylammonium polymethacrylate, being formed [3]. Secondly, it
has been found that the ion-exchange properties of amphoteric resins
were often superior when the acid precursor, MAm, was used [4].
We were therefore interested in studying the structure and properties
of the water-soluble analogs.

Butler and his co-workers [5] have reported the radical-initiated
cyclopolymerization of dialkyldiallylammonium halides and diallyl-
amine hydrochloride. Other workers [6] have reported the cyclo-
polymerization of RDAA·HCl using ammonium persulfate as initiator
in dimethyl sulfoxide. However, in the latter study the yield of
polymer was always less than 30%.

In this paper are reported the results of examining the effect of a
number of different solvents and initiators on the polymerization of
RDAA·HCl and also the results of attempts to form copolymers with
MAm. In common with the observations of others [7], it was found
that the free base form of the amines, diallylamine and RDAA, did
not polymerize to any significant extent under any of the conditions
used in this study.

RESULTS AND DISCUSSION

Poly-RDAA

The preparation and properties of some homopolymers of RDAA
are summarized in Tables 1 and 2.

Solubility

According to the cyclic polymerization scheme proposed by Butler [5], alkyldiallylamines should polymerize to linear soluble polymers except, perhaps, at very high concentrations [8]. The solubility characteristics of the majority of the polymers made in this study are in accord with this scheme (Table 2) although sometimes a gel was formed on standing at room temperature.

Yields

The yield of linear polymers was usually very good, whether prepared by γ-irradiation or by azobisisobutyramidinium dichloride (amido) initiation. The yield and properties of a polymer prepared by either amido or γ-initiation were always comparable. The yields generally decreased as the size of the alkyl substituent was increased. Ammonium persulfate (APS) and azobisisobutyronitrile (AIBN) were found to be very poor initiators.

pKa Values

The pKa value (which was taken as the pH at half neutralization) for all polymers was found to be much lower than that for the corresponding saturated pyrrolidine, piperidine, or aliphatic tertiary amine. This may be the result of a combination of the polyelectrolyte effect and the insolubility of the polymers in their free-base forms. Since polymethyldiallylamine is the most soluble of the polymers, it is reasonable to expect it to have the highest pKa value.

Structure of Poly-RDAA

Analyses. Some typical analytical figures are given in Table 3. Although the resins were dried at 50° C in vacuo for as long as one week, they all still contained oxygen, a result which is most likely caused by occluded water. The majority of the poly-RDAA·HCl were hygroscopic; poly(methyldiallylamine hydrochloride) was very hygroscopic.

IR Spectra. Infrared spectral characteristics of the poly-RDAA may be illustrated by those for polymethyldiallylamine (poly-MDAA). The spectra of the other polymers were similar. Some of the more significant bands for the monomer and polymer as the free bases and as the hydrochlorides are listed in Table 4. The bands at ca. 3500 and 2700 cm^{-1} are due to water and the trialkylammonium ion, respectively. The bands at 970 and 920 cm^{-1} for MDAA and 950 cm^{-1} for MDAA·HCl were assigned to the CH out-of-plane deformations of

TABLE 1. Properties of Some Poly-RDAA

Polymer	R in amine, $RN(CH_2CH=CH_2)_2$	Solids content (%)[a]	Polymerization time (hr)	Polymerization temp (°C)	Initiator[b]	Yield of pure polymer (%)	pKa Monomer	pKa Polymer
M-1	Methyl	19	20	65	APS	<10	9.0[c]	9.5[d]
2	"	60	65	65	amido	90		9.5[d]
3	"	38	65	65	amido	90		9.5[d]
4	"	60	—	—	γ	90		gel
5	"	38	—	—	γ	90		9.45[d]
P-1	n-Propyl	f	96	65	APS	<34	8.8[e]	8.8[e]
2	"	60	65	65	amido	92		8.88[e]
3	"	60	—	—	γ	90		8.8[e]
4	"	72	—	—	γ	part gel		gel
B-1	Benzyl	60	48	60	amido	50	6.15[e]	6.65[e]
2	"	60	—	—	γ	50		6.50[e]
H-1	n-Hexyl	60	65	65	APS	8	—	—
2	"	60	65	65	amido	70	7.0[e]	7.13[e]
3	"	60	—	—	γ	70		7.0[e]

T-1	Allyl	10	48	65	amido	40	—	—
2	"	~60	—	—	γ	50	8.3	9.0

[a]Solvent was water in each case.
[b]APS = ammonium persulfate, 1.9 mole %; amido = azobisisobutyramidinium dichloride, 1.9 mole %;
γ = γ-irradiation from cobalt-60.
[c]Solution clear during whole of the titration.
[d]Solution turned turbid after half-neutralization.
[e]Solution turned turbid before half-neutralization.
[f]Skew addition of monomer over 4 days; solids content varied from 38 to 18%.

TABLE 2. Solubility of Some Poly-RDAA

Sample	Solvent[a]							
	Water	Acetone	Methanol	Chloroform	Benzene	Ether	Hexane	Petroleum ether
MDAA free base monomer	i	s	s	s	s	s	s	s
Poly-MDAA/FB	i	p	s	s	p	p	i	i
Poly-MDAA·HCl	s	i	s	i	i	i	i	i
PDAA/FB monomer	i	s	s	s	s	s	s	s
Poly-PDAA/FB	i	p	s	s	s	p	p	s
Poly-PDAA·HCl	s	i	s	i	i	i	i	i
BzDAA/FB monomer	i	s	s	s	s	s	s	s
Poly-BzDAA/FB	i	p	p	s	s	p	p	i
Poly-BzDAA·HCl	p	i	s	i	i	i	i	i

[a]Solubility: s = soluble; p = partly soluble; i = insoluble.

TABLE 3. Analytical Values for Some Poly-RDAA·HCl

Polymer		C (%)	H (%)	N (%)	O (%)	Cl (%)
M-2	Calcd for $C_7H_{14}NCl$:	56.94	9.49	9.49	–	24.06
	Found:	54.98	10.08	9.82	3.8	23.1
P-2	Calcd for $C_9H_{18}NCl$:	61.50	10.26	7.98	–	20.23
	Found:	60.56	10.37	8.15	2.7	19.1
H-2	Calcd for $C_{12}H_{24}NCl$:	66.20	11.03	6.43	–	16.32
	Found:	63.46	10.73	6.47	3.3	15.3

TABLE 4. Some Significant IR Bands

Compound			Band (cm^{-1})			
MDAA·HCl	3550	2700	1640-1620		950	
MDAA	–	–	1640	970		920
Poly-MDAA·HCl	3500	2700	1670 1620			
Poly-MDAA	–	–	1670-1620			

the unsaturated allyl group. The sharp intense band at 1640 cm^{-1} for MDAA is attributed to the C=C stretching of the allyl group. The bands at 970, 920, and 950 cm^{-1} disappeared in the polymer but there were always bands at 1620-1650 cm^{-1} even in a polymer where no unsaturation could be detected by other means such as NMR spectroscopy. The presence or absence of bands between 900 and 1000 was therefore subsequently taken as evidence for the presence or absence of unsaturation in a polymer. The disappearance of the allyl peak at 1640 cm^{-1} was found to be replaced by a new peak in a similar range. The cause of this latter peak may be an amide group although the concentration of the amide must be small since the base capacity of the polymer is not significantly diminished.

NMR Spectra. Although several NMR and IR spectra of a polymer suggested the presence of unsaturation it was possible eventually to remove all evidence of unsaturation by continuous acetone extraction of the poly-RDAA·HCl. It is significant to note that the protons α to the nitrogen atom in the free base form of the polymers were
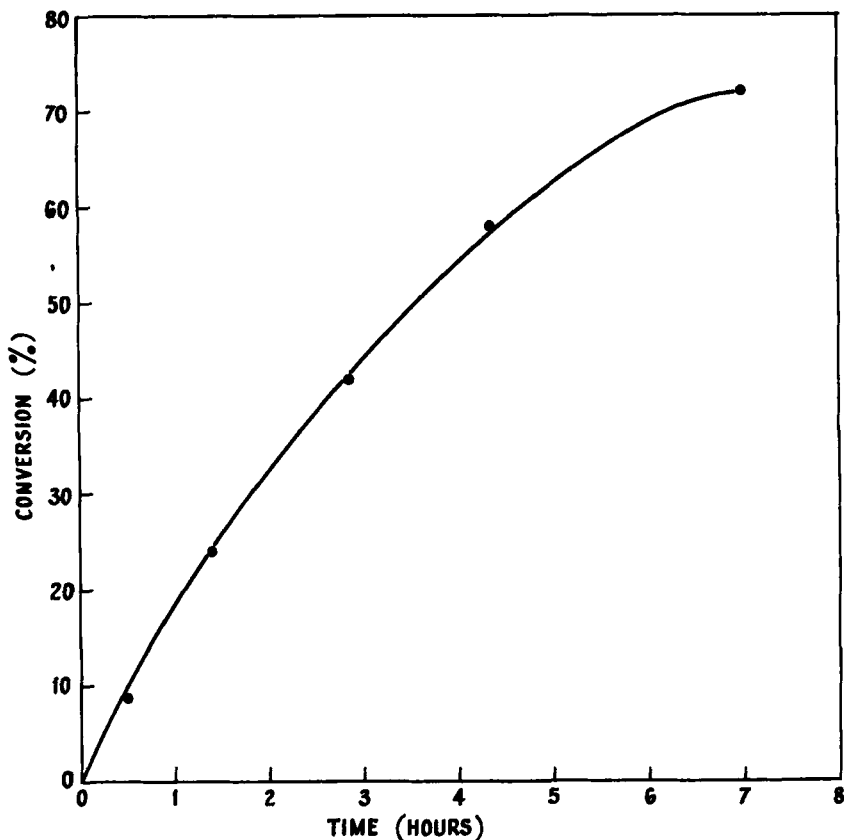
FIG. 1. Percentage conversion of MDAA·HCl to poly-MDAA·HCl (as a 38% solution in D_2O at 65°C with 2 mole % amido).

nonequivalent. Such nonequivalence is indicative of ring structures, the most likely being five-membered rings [8]. The magnitude of the chemical shift difference depended on the nature of the nitrogen substituent. It was not possible from proton NMR spectra of these polymers to distinguish between the possible alternative ring systems. However, ^{13}C NMR spectra of poly-MDAA and poly-BzDAA are consistent with a five-membered ring structure in which the ratio of cis to trans isomers is about 4:1.

Since very characteristic changes occur in the NMR spectrum of

TABLE 5. Molecular Weights of Poly-RDAA

| Polymer[a] | MW of hydrochloride in methanol | MW of free base | |
		In methanol	In chloroform
M-2	730	—	—
M-3	450	—	—
M-3A[b]	1200	—	2600
M-4	gel	—	—
M-5	700	—	—
M-6[c]	—	—	1500
P-1	450	—	—
P-2	850	1800	3100
P-3	1450	—	—
H-2	1400	—	—
H-3	1670	—	—
B-1	1450	—	3300
B-2	1640	—	—

[a]See Table 1 for other details of polymers.
[b]Same as M-3 except prepared on 7 times the scale of M-3.
[c]Similar to M-3 except solids content was 25%.

an amine hydrochloride during its polymerization, the rates of polymerization of some RDAA in D_2O using amido as the initiator were thus conveniently followed by NMR spectroscopy. The rate of polymerization of MDAA·HCl (Fig. 1) was found to be first-order in monomer concentration as expected for a chain polymerization reaction.

Molecular Weights (MW). Molecular weights were measured by using a vapor pressure osmometer and some representative values are given in Table 5. It is important to realize that the MW of a poly-RDAA·HCl measured in methanol is only an apparent value and is dependent upon the degree of dissociation of the polymer. The observation that the apparent MW of a poly-RDAA·HCl in methanol was found to be between one half and one quarter of the MW found for the same polymer as its free base in chloroform is in accord with the expected

dissociation of the polymer [9]. Values of MW closer to the "true" MW should be obtained from measurements on the free base. However, the MW of the free bases measured in methanol and chloroform were less reproducible than those measured on the hydrochloride in methanol. Uncertainties in the MW of the free bases may be the result of the occurrence of some of the reactions responsible for subsequent gelation.

Several observations may be made from the relative values of the apparent MW of the hydrochlorides given in Table 5. For a given set of experimental conditions the MW and the degree of polymerization for polyhexyl-DAA and polybenzyl-DAA was found to be greater and the yield of polymer lower than for poly-MDAA and poly-PDAA. For a given solids content, the MW of a polymer prepared by γ-irradiation was greater than that prepared by amido initiation which, in turn, was greater than that prepared by APS initiation. It should be possible to interpret these results from a knowledge of the initiating radical concentration. Although 1.9 mole % of both APS and amido was used, the half-life of APS is more than twice that of amido. However, it is not possible to calculate the concentration of the initiating radical, especially in the case of APS in view of its controversial mechanism of decomposition [10]. For a given monomer and initiation conditions, the MW increased as the solids content of the monomer was increased. The MW of a polymer was found to depend on the scale on which a polymerization was performed. Thus increasing the scale of the reaction gave a higher MW polymer. This observation is consistent with oxygen inhibition, since larger-scale experiments would have a relatively smaller surface area exposed to the atmosphere. The observation may also be due in part to higher temperatures within a part of the solution caused by less efficient mixing.

Gelation of Poly-RDAA

At high solids content it was occasionally observed that a gel rather than a linear soluble polymer was obtained. In other cases, although a soluble polymer was obtained initially, the polymer stored as the free base in solution or in the solid state gelled. The fact that the MW of the polymer as its free base increased with time is clearly demonstrated in Fig. 2. The MW of the hydrochloride remained unchanged after several months.

A study of the gelation phenomena could be useful from several points of view. It could lead to a better understanding of the polymerization mechanism and of the structure of the final product and also the linear polyamine may graft and/or initiate further polymerization with another monomer such as an allyl compound or
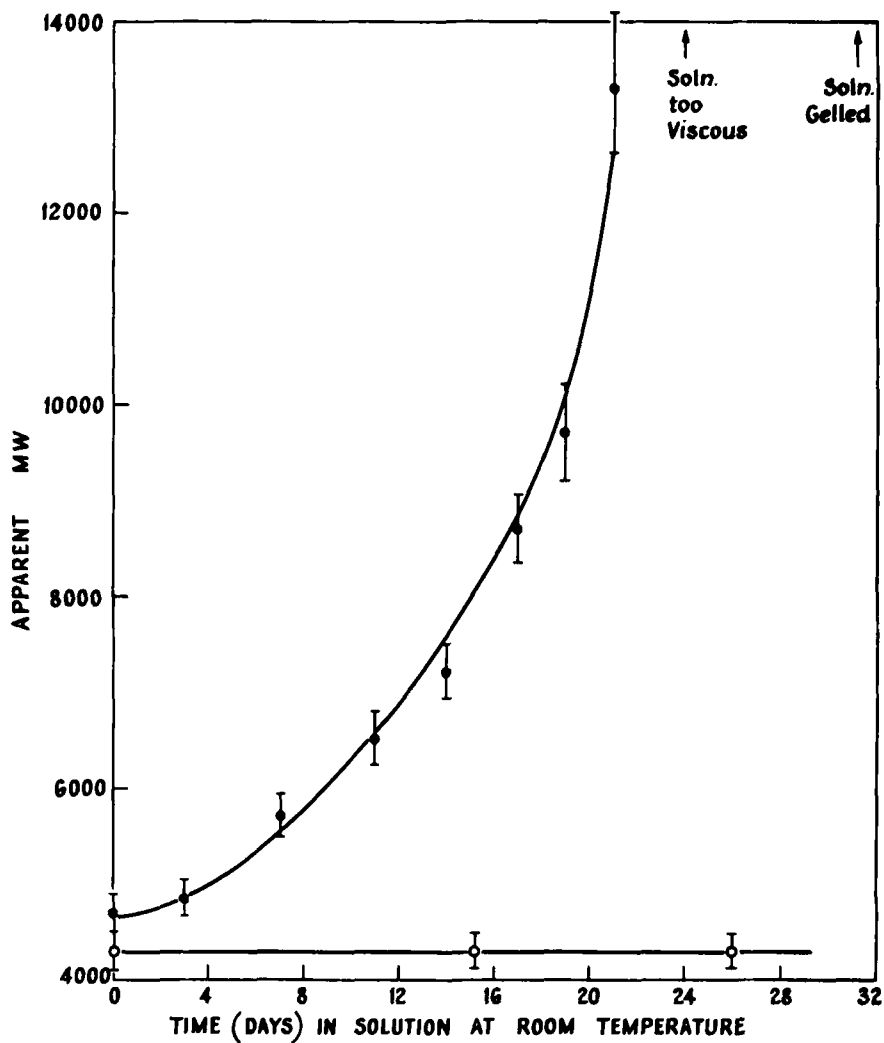
FIG. 2. Change in MW of poly-MDAA on standing (as a 4% solution in chloroform): (●) poly-MDAA; (○) poly-MDAA·HCl (in methanol).

methacrylamide. Although at least in the latter case a linear poly-
diallylamine and methacrylamide "copolymerized" spontaneously
after several months, the gel was so soft as to be of no practical
value.

The results of an extensive investigation of the gelation phenomena
may be summarized as follows.

(1). Once a linear polymer had been prepared it did not gel unless
converted to the free base. However, polymers prepared at high con-
centrations on a large scale (polymers were always made from the
amine hydrochloride) sometimes gelled during their preparation. It
may be that two different types of gelation reactions are occurring.
In the latter, the unsaturated groups could be involved. During the
polymerization, three major reactions may compete in the chain-
growth step as shown in Eq. (1) [8], where Z is the initiator fragment.
Although in these systems cyclization (reaction 2) is generally greatly
favored over propagation of the uncyclized radical (reaction 1) at very

$$(1)$$
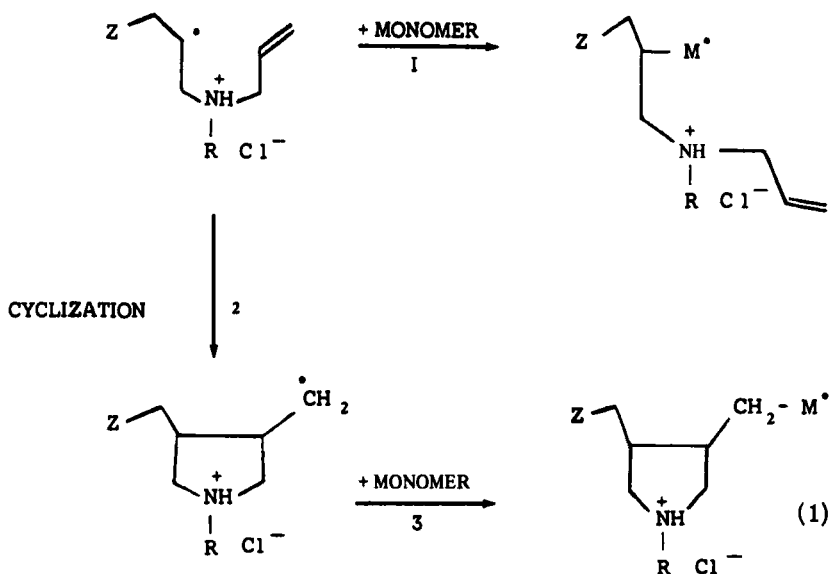
high monomer concentrations the relative ratio of reactions 1 and
2 can be altered sufficiently to allow for greater amounts of reaction 1
to occur and the possibility of crosslinked polymer forming.

Repeated solvent extraction of the polymers gave products in which

no evidence could be found by IR spectra or NMR spectroscopy for unsaturation. Also, no radicals could be detected in the polymers by ESR spectroscopy yet these polymers when converted to their free base form, gelled on standing. We are unable to write any polymerization schemes which yield products which are both free of unsaturation and free radicals and yet possess reactive centers capable of promoting further reaction.

(2) The rate of gelation of the free base is not accelerated by heat.

(3) Hydroquinones reduce the rate of gelation of the free base.

(4) This would suggest a radical mechanism for the gelation reaction, but the addition of amido or AIBN to a solution of the free base and heating does not accelerate the rate of gelation.

(5) The addition of monomer reduces the rate of gelation of the free base.

(6) The yield of the gel is very high. Once the solution has gelled, very little soluble material can be extracted from the gel.

(7) The fact that the free base does not exist as a microgel in solution which subsequently forms a macrogel, was shown by filtration of a solution of the free base through a 0.45 μm Millipore filter.

(8) Quarternization is not responsible for the gelling phenomena.

It was found that solutions of the free base in methanol or chloroform reacted rapidly with dibromo and dichloro compounds to yield gels very similar in physical properties to those observed on spontaneous gelation. If hydrogen chloride had added across an allyl group then the halo derivative could react with the nitrogen to form a gel. However, experiments showed that hydrogen chloride does not add to the allyl group under the conditions used in the polymerizations. Furthermore, free bases extracted with benzene or butanol were free of chloride but still gelled as readily as those extracted with chloroform. Similarly, polymers prepared from the amine sulfate were also found to gel.

The above observations would be consistent with the involvement of oxygen in the gelling phenomena. It is well known that amines are much more readily oxidized in neutral or basic media than under acid conditions and gelling was observed only for the polymer in its free base form. Oxidation by atmospheric oxygen would appear to be the most likely explanation for the band at 1670 cm^{-1} (Table 4), which was attributed to an amide group, in the IR spectra of these polymers. A similar band at 1670 cm^{-1}, also attributed to an amide group, has recently been reported in the IR spectra of a sample of polyethylenimine oxidized by hydrogen peroxide [11]. The mechanism of the amide formation for the poly-RDAA must be different from that proposed for polyethylenimine, since the latter involves

TABLE 6. "Copolymers" of

Diallyl-amine	Poly-mer no.	Molar ratio MAm: amine HCl	Solvent	Total solids content (%)	Initiator (mole %)	Isolation procedure
Propyl	1	2:1[a]	H_2O	29	APS (1.9)	Freeze dried
"	2	2:1	H_2O	29	γ	"
"	3	1:2	H_2O	39	APS(1.9)	"
"	4	2:1	Dioxane	29	"	"
"	5	2:1	DMF	47	γ	Filtration
"	6	2:1	"	47	AIBN(2)	"
Methyl	7	2:1	H_2O	53	amido(2)	Freeze dried
"	8	1:1	H_2O	53	"	"
"	9	1:2	H_2O	53	"	"
Propyl	10	2:1	H_2O	29	APS(0.9)	Precipitate with NaOH solution
"	11	2:1	H_2O	29	APS(1.9)	
"	12	2:1	H_2O	29	APS(3.7)	

[a]Skew addition of MAm over a period of 4 days.
[b]Solution turned turbid before half-neutralization.

a secondary amine and the former a tertiary amine. Further, the mechanism of initiation of the gelling phenomena must be different again but would probably involve attack at the γ carbon atom.

Copolymerization Studies of N-alkyl-N,N-diallyl-amines (RDAA) and Methacrylamide (MAm)

The polymerization conditions and some of the properties of the polymers are summarized in Table 6. Attempts to isolate the polymeric product in its free base form by precipitation with ammonia or sodium

Methacrylamide (MAm) and RDAA

| Purification procedure | Yield (%) | | Properties of the "copolymer" | | | |
	Based on total monomer	Based on MAm used	Amine in polymer (mole %)	Amine in polymer (wt %)	pKa of amine group	MAm in polymer (wt %)
Methanol extraction	44	90	17.7	31	9.72[b]	69
"	49	90	13.3	24	9.7[c]	76
"	17	85	16.7	29	9.5[c]	71
"	50	95	10.2	19	9.7[c]	81
"	58	100	9.3	17.5	9.9[d]	82.5
"	49	100	11	19	9.9[c]	81
"	60	100	13	21	9.5[c]	79
"	49	100	24	35.5	9.4[c]	64.5
"	13	60	29	41	9.3[c]	59
None	45	90	–	–	–	–
"	50	100	–	–	–	–
"	50	100	–	–	–	–

[c]Solution turned turbid after half-neutralization.
[d]Solution clear during whole of titration.

hydroxide solutions were unsatisfactory. It was found that the polymeric product as its hydrochloride could be conveniently isolated by either freeze-drying (if water was used as the solvent) or filtration (if an organic solvent was used). Since all poly-RDAA·HCl and RDAA·HCl are readily soluble in methanol, the polymeric product was purified by extraction with methanol to give a methanol-insoluble fraction hereafter designated the "copolymer." The "copolymer" could also be purified by dialysis for 24 hr. For a given polymer preparation, the material remaining inside the dialysis tubing after this time was usually identical to the methanol-insoluble fraction.

Methanol-Soluble Fraction. The properties of the methanol-soluble fractions (or the fractions which passed through the dialysis tubing) were investigated by the techniques outlined above for the homopolymers of RDAA·HCl. The properties of the methanol-soluble fractions were those expected for mixtures of poly-RDAA·HCl and RDAA·HCl although it was common to find as much as 30% MAm residues present, probably as a low molecular weight homopolymer. The methanol-soluble fractions of polymers 1, 3, 4, and 6 contained greater than 90% of unchanged amine hydrochloride monomer. The methanol-soluble fractions of polymers 2, 5, and 7-9 contained greater than 75% poly-RDAA·HCl. These results are consistent with the fact that the amido initiator is the best chemical initiator of those studied here for the polymerization of diallylamine hydrochlorides.

Microanalyses. Microanalyses could not be used to determine accurate "copolymer" compositions because both components contained nitrogen. However, the choice of alternative comonomers for the RDAA·HCl was limited by the solubility requirements of the monomers. Both the RDAA·HCl and MAm are readily soluble in water.

Two further factors which reduce the value of elemental nitrogen analysis of a "copolymer" from diallylamine hydrochlorides and MAm for the determination of the "copolymer" composition are the hydrolyses of some of the amide groups and imide formation. Imide formation is induced both thermally and by strong mineral acids [12]. Although sufficient hydrolyses and imide formation occurs to complicate the determination of the "copolymer" composition from the nitrogen analysis, it was found that hydrolysis of the MAm "copolymers" never exceeded about 55%, even by heating with a 4 $\underline{N}$ sodium hydroxide solution at 98°C in a steel bomb for one week. Thus, the capacity of any "copolymer" containing MAm, after hydrolysis, cannot exceed about 66% of that theoretically available. These findings are in agreement with those of Arcus [13]. It has recently been reported that even polyacrylamide reaches a hydrolysis conversion limit at about 60% hydrolysis [14].

Yield of "Copolymer." An inspection of Table 6 indicates that in general the yield of "copolymer" is approximately equal to the weight of MAm used in the polymerization. In other words, the yield based on the weight of MAm used is about 100%. The percentage of amine incorporated into the "copolymer" increases with an increase in the amine:MAm ratio in the monomer feed and thus, from above, the yield of "copolymer" decreases.

The composition of a "copolymer" was determined by a silver nitrate titration (chloride content) and sodium hydroxide titration of a "copolymer" solution.

The yield and composition of a "copolymer" when prepared in water was found to be relatively insensitive to the mode of initiation (APS, amido or γ-irradiation). In fact, the incorporation of amine into the "copolymer" was slightly lower when γ-irradiation was used. Amido as an initiator results in a slightly better yield of "copolymer" with a lower amine incorporation compared with APS (polymers 1, 7-9).

The yield of the "copolymer" was found to be independent of the concentration of APS (polymers 10-12).

No beneficial effect on the yield or amine composition of the "copolymer" was observed by substituting an organic solvent such as dioxane or DMF for some, or all, of the water. In general, the amine content of a "copolymer" prepared in dioxane or DMF was lower than the analogous "copolymer" prepared in water.

Evidence for Formation of "Copolymer." As has been discussed above, RDAA·HCl and poly RDAA·HCl are soluble in methanol, but the "copolymer" is insoluble in methanol. It may be that failure to extract all the polyamine is a result of physical interaction between the two homopolymers.

Continued dialysis of the "copolymer" for periods in excess of 24 hr resulted in a slow loss of the "copolymer" with the amine content remaining constant. Therefore either the true copolymer was dialyzing out, or MAm homopolymer and RDDD·HCl homopolymer dialyze out at the same rate (see Tables 7 and 8).

The pKa of the amine group in the "copolymer" of PDAA and MAm was found to be 9.7-9.9, which is about 1.0 pKa unit more basic than that of both PDAA and poly-PDAA (Table 1). This difference would appear to indicate that the amine group is present in a true copolymer. However, the validity of such an argument is questionable since the poly-PDAA goes turbid during its titration before the point of half-neutralization, and therefore the pKa is probably greater than the apparent pKa. On the other hand, solutions of the PDAA:MAm "copolymer" generally remain clear until after half-neutralization.

The argument that the solubility properties are responsible for the observed pKa effects rather than the existence of a true copolymer is supported by a consideration of the "copolymers" of MDAA and MAm. In this case the pKa of the amine group in the "copolymer" is about 9.4 (Table 6) which is almost identical to that of poly-MDAA (Table 1). Each of these systems remains clear until after the half-neutralization point.

Evidence for a Mixture of Homopolymers. It was found that IR and proton NMR spectral evidence was inadequate for determining whether a true copolymer or a mixture of homopolymers had been formed. The IR and NMR spectra of most of the "copolymers"

TABLE 7. Effect of Duration of Dialysis on the Properties of a "Copolymer"

Sample no.[a]	Dialysis		Wt loss (%)	Amine/ (meq/g)[b]	pKa
	Initial pH	Time (hr)			
13	—	—	0	1.75	9.7[c]
14	5	24	52	2.0	9.8[c]
15	5	65	75	2.3	9.7[c]
16	12	24	32	2.0	9.4[d]
17	12	65	37	1.9	9.3[d]

[a]Prepared with APS as initiator and MAm added over a period of 4 days. No purification prior to dialysis.
[b]All capacities in this paper are expressed as meq/g of "copolymer" in the hydrochloride form.
[c]Solution became turbid after half-neutralization.
[d]Solution became turbid before half-neutralization.

TABLE 8. Results of Some Dialysis Experiments on Some "Copolymers"

Sample no.[a]	Hydrolysis time (days)[b]	Dialysis		Wt loss (%)	Amine (meq/g)	CO_2^- (meq/g)	pKa
		Initial pH	Time (hr)				
4	0	—	—	0	1.08	—	9.7[c]
4	0	5	65	59	1.05	—	9.9[d]
5	0	—	—	0	1.0	0	9.9[d]
5	0	5	24	27	1.0	0	9.9[d]
5	0	12	24	22	1.2	0	9.9[d]
5	2	4.9	24	17	<0.3	5.6	5.6
5	2	>13	24	75	<0.3	4.9	5.7

[a]See Table 6; all purified by methanol extraction.
[b]Hydrolysis in 4 N NaOH solution at 98° C.
[c]Solution turned turbid after half-neutralization.
[d]Solution clear during whole of titration.

were indistinguishable from those of poly-MAm. In those cases where larger amounts of amine were present, peaks characteristic of the polyamine were superimposed upon those of the polyMAm.

The dialysis of polymer 4 (Table 8) for 65 hr resulted in a loss of a 59% of the polymer, but the amine content remained constant at 1.05 meq/g. Similarly, the dialysis of polymer 5 (Table 8) at an initial pH of either 5 or 12 resulted in a loss of 27 and 22%, respectively, after 24 hr, but the amine composition of the remaining "copolymer" remained constant. On the other hand, dialysis of a hydrolyzed sample of polymer 5 (Table 8) resulted in a rapid loss of the amine relative to MAm (or its hydrolyzed equivalent). Furthermore, the rate of dialysis depended on the initial pH of the solution. It can be seen that the unhydrolyzed "copolymer" dialyzed more rapidly at low pH, whereas the hydrolyzed copolymer dialyzed more rapidly at high pH.

The amine content of the hydrolyzed "copolymers" after dialysis was estimated from potentiometric titrations and generally no amine endpoint could be detected. Although the failure to observe an amine endpoint may be due to the new "copolymer," it appears more likely that hydrolysis and dialysis resulted in a preferential loss of the amine. One interpretation of these results is that the amine forms a copolymer by grating onto the amide group which, on hydrolysis, is cleaved to give two homopolymers. However, no evidence of grafting could be detected in the homopolymerization of MDAA·HCl in the presence of propionamide.

EXPERIMENTAL

Materials

The N-alkyl-N,N-diallylamines (RDAA) were prepared from allyl chloride and the corresponding amine [6]. Benzyldiallylamine was prepared from benzyl chloride and allyl amine. Methacrylamide was obtained from K and K Laboratories Inc., and used without purification. 2,2'-Azobisisobutyramidinium dichloride (amido) was prepared by the addition of ammonia to the imino ether of 2,2'-azobisisobutyronitrile [15]. Ammonium persulfate (APS) (Cyanamid) and 2,2'-azobisisobutyronitrile (AIBN) (Fluka, purum) were used without purification.

All solvents were of analytical reagent grade.

Instrumentation

Infrared (IR) spectra were recorded on a Perkin-Elmer grating
257 infrared spectrophotometer as KBr disks or Nujol films. Proton
nuclear magnetic resonance (NMR) spectra were recorded on a
Varian T-60 NMR spectrometer in approximately 10% solutions or
on a Varian HA-100 spectrometer.

^{13}C NMR spectra were recorded on approximately 20% solutions
on a HX00 Bruker spectrometer.

Molecular weights were measured by using a Mechrolab Model
301A vapor pressure osmometer. The solvent was either methanol
or chloroform and benzil was used to calibrate the instrument.

The pH measurements were made by using a Metrohm Herisau
pH-Meter E520 which was calibrated at pH 4 and 7.

Polymerizations

Polyamines (Poly-RDAA)

The experimental conditions for the preparation of the polyamines
are summarized in Table 1. All chemically initiated polymerizations
were done under nitrogen. All polymers prepared by γ-irradiation
received the same total dose (10 Mrad) at a dose rate of ca. 0.3
Mrad/hr.

The polymers were isolated by freeze drying and purified by Soxhlet
extraction with acetone for periods of up to one week. It was found
that all RDAA·HCl polymers were insoluble in dry acetone and all
monomer hydrochlorides were soluble. The polymers were dried in
vacuo at 50°C for several days. The RDAA·HCl polymers were all
obtained as light pink, crystalline solids and their free bases as
light yellow, glassy materials. The latter were therefore more dif-
ficult to handle. No suitable solvent could be found for extracting
the monomer in the free base form from the polymer in the free base
form.

Typical analytical and IR spectral data for some polyamines are
given in Tables 3 and 4, respectively. Some typical NMR spectral
data are as follows. For poly-MDAA·HCl (in D_2O), δ=3.05 (singlet,
3 protons, N-methyl), δ = 3.55 (broad multiplet, 4 protons, methylenes
adjacent to nitrogen), δ = 2.6 (broad multiplet, 2 protons) and δ = 1.55
(broad multiplet, 4 protons) and for poly MDAA (in $CDCl_3$) δ = 2.33
(singlet, 3 protons, N-methyl), δ = 2.3 and 3.05 (broad multiplets,
2 protons each, methylenes adjacent to nitrogen), δ = 2.05 (broad
multiplet, 2 protons) and δ = 1.4 ppm (broad multiplet, 4 protons).

For poly-BzDAA (in CDCl₃), δ = 7.33 (singlet, 5 protons, aromatic protons), δ = 3.3 (singlet, 2 protons, benzylic protons), δ = 2.03 and 2.98 (broad multiplets, 2 protons each, methylenes adjacent to nitrogen), δ = 2.03 (broad multiplet, 2 protons) and δ = 1.21 ppm (broad multiplet, 4 protons).

Copolymers of Diallylamines (RDAA) and Methacrylamide (MAm)

Polymerizations. All polymerizations were carried out under nitrogen and all chemically initiated polymers prepared by heating at 65°C for 4-65 hr. The monomer ratios, solvent, initiator, and other polymerization conditions are summarized in Table 6. All polymerizations performed with γ-irradiation received the same total dose (10 Mrad) at a dose rate of ca. 0.3 Mrad/hr. All polymerizations initiated by APS were carried out in the presence of 200 ppm EDTA [16].

Isolation and Purification. The procedures of isolation and purification are detailed in the discussion. Visking Company cellulose casing dialysis tubing was used in the dialysis experiments.

CONCLUSIONS

The polymerization of MAm in the presence of RDAA·HCl initiated by chemical means or by γ-irradiation gives predominantly a mixture of homopolymers. The yield of methanol-insoluble material was usually about 100% based on the amount of MAm in the monomer feed. MAm is very easily polymerized by a variety of initiators, and the major effect of polymerization in the presence of RDAA·HCl is to reduce the rate of polymerization of MAm. Although some true copolymer is probably formed, it appears likely that much of the "copolymer" consists of an entanglement of homopolymers.

In copolymerizations with APS or AIBN, two initiators which are ineffective for the homopolymerization of RDAA·HCl, a greater amount of amine was found to be incorporated into the "copolymer" than would have homopolymerized in the absence of MAm. We are not at present able to explain this result, but from a practical point of view it could mean that initiators which are unsuitable for homopolymerizations of RDAA·HCl may, nevertheless be suitable for copolymerizations with acid precursors.

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