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Thermally Regenerable Ion-Exchange Resins by Photografting

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ABSTRACT

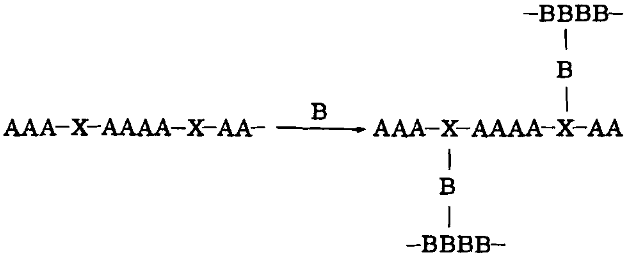
Crosslinked polymer beads containing regions of acidic and basic groups are the preferred structures for the efficient operation of a thermally regenerable ion-exchange process. Such systems can be prepared by various methods. Here the approach of using polymers and copolymers containing photolabile groups as grafting sites is described. The polymers studied were polytriallylamine hydrochloride (polyTAA) and copolymers of propyldiallylamine hydrochloride (PDAA) and allyl benzoin methyl ether (ABME), of ABME and acrylic acid (AA), and of ABME and methyl acrylate (MA). The maximum amount of photografting of MA onto polyTAA was

12%. Very little photografting of MA onto PDAA:ABME copolymers was obtained. Photografting of TAA to AA:ABME and to MA:ABME copolymers occurred readily by using radiation of 360 nm wavelength, with the best yields of photografted polymer being about 60% when a MA:ABME copolymer was irradiated in a suspension. The effect of suspending medium, stirring rate, irradiation time, irradiation intensity, solvent, solids concentration, percentage of ABME in the MA:ABME copolymer, additional crosslinkers, surfactants, and the acid:base ratio in the hydrolyzed resin prepared by photografting TAA onto MA:ABME copolymers on the yield, physical strength, shape, and ion-exchange properties of the resins is reported.

INTRODUCTION

The Sirotherm plant for the partial demineralization of low salinity waters uses a mixed bed of weak acid and weak base resins which are regenerated by washing with hot water [1]. (Sirotherm is the ICI Australia Limited registered trade mark for thermally regenerable ion-exchange resins and associated plant.) The problem of the slow rate of salt adsorption by a mixture of conventional size ion-exchange resins may be overcome by the "plum-pudding" concept [2], in which basic and acidic micro particles are embedded together in a water- and salt-permeable inert matrix to give a composite bead of conventional size. However, a considerable proportion of the resin bead was then inert binder, and therefore the preparation of so-called "no-matrix" resins was explored [3]. In the idealized structure of a no-matrix resin the final bead size should be about 1 mm in diameter with discrete acidic and basic domains of size 0.01-5 μm [4]. Such no-matrix resins have the potential of higher thermally regenerable capacities because of the absence of inert matrix, should be rapidly reacting, and, in the simplest situation, could be prepared in one reaction step from two appropriate monomers.

No-matrix resins have been prepared by polymerizing a mixture of monomers [3, 4], and electron micrographs of the resins show them to be composed of discrete acidic and basic domains [4]. However, no evidence could be obtained to show whether copolymers or a mixture of homopolymers had been formed. Some copolymerization studies of N-alkyl-N,N-diallylamines and methacrylamide indicated that mainly a mixture of homopolymers is formed [5]. It was therefore of interest to prepare no-matrix resins in which grafting between the acidic and basic domains is controlled by the method of polymerization. One way of ensuring grafting would be to use a prepolymer 1, containing grafting sites X [Eq. (1)] which could be activated to initiate the polymerization and grafting of the monomer B.



$$\text{AAA-X-AAAA-X-AA-} \xrightarrow{\text{B}} \text{AAA-}\underset{\substack{|\\ \text{B}\\ |\\ \text{-BBBB-}}}{\text{X}}\text{-AAAA-}\overset{\substack{\text{-BBBB-}\\ |\\ \text{B}\\ |}}{\text{X}}\text{-AA} \qquad (1)$$

Prepolymer 1

This paper reports the results of studies in which ultraviolet radiation was used to activate the group X. Acrylic acid or methyl acrylate was chosen as the acid or acid precursor component, and allylamines (usually, triallylamine) as the base component. The three different prepolymers containing potential grafting sites examined were polytriallylamine, a copolymer of diallylamines and an unsaturated benzoin derivative and a copolymer of acrylic acid (or its ester) and an unsaturated benzoin derivative. Photochemical grafting of methyl acrylate, methyl acrylate, and triallylamine, respectively, was studied.

RESULTS AND DISCUSSION

Grafting to Polytriallylamine

Triallylamine undergoes cyclopolymerization [6] to give polymers containing mainly five-membered ring structures [7] with the pendent allyl group giving rise to crosslinking. However, such polymers always contain some unsaturation, and it has been shown that there is usually one free allyl group for every 2.5 to 3.0 nitrogen atoms [8]. These free allyl groups should be a source of further reaction if they can be activated by UV irradiation. Irradiation of polytriallylamine at 360 nm in the presence of methyl acrylate and the sensitizer methyl benzoin methyl ether (MBME) or at 254 nm in a quartz vessel resulted in no grafting (Table 1). An unwashed sample of polytriallylamine contains not only crosslinked polytriallylamine but also some linear polytriallylamine, which is richer in unsaturation.

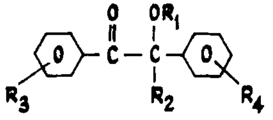
TABLE 1. Photografting of MA to PolyTAA·HCl

Polymer	Monomer	λ (nm)	Sensitizer	Grafting (%)
Unwashed PTAA.HCl	MA	360	MBME	0
Washed PTAA.HCl	MA	360	MBME	0
Unwashed PTAA.HCl	MA	254	None	12
Washed PTAA.HCl	MA	254	None	0

Table 1 shows that irradiation of the unwashed polymer in the presence of methyl acrylate at 360 nm with methyl benzoin methyl ether as sensitizer resulted in no grafting, while irradiation at 254 nm in a quartz vessel resulted in a 12% graft which is too small to be of practical importance. It thus appears that no significant grafting of methyl acrylate onto polytriallylamine occurs on irradiation at wavelengths greater than 300 nm.

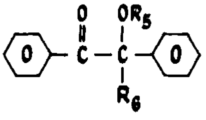
Grafting to Copolymers Containing Benzoin Derivatives

In general, group X in prepolymer 1 [Eq. (1)] could be a number of possible photolabile groups [9, 10]. However, di- and triallylamines are difficult to polymerize [11], and it has been found that benzoin alkyl ethers are usually superior to other photosensitizers studied for the photopolymerization of allylamines [12]. Therefore, prepolymers of type 1 were prepared in which group X was derived from an unsaturated benzoin derivative of which several suitable structures are shown. When a benzoin alkyl ether is irradiated, it may undergo



R_3 or R_4 = vinyl

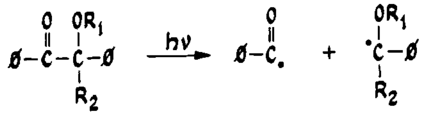
R_1 and R_2 = H or alkyl



R_5 = H or alkyl

R_6 = vinyl or allyl

homolytic fission [Eq. (2)] to form two radicals, a benzoyl radical I and an alkoxybenzyl radical II. Either or both of these radicals may



$$\phi-\overset{O}{\overset{\|}{C}}-\underset{R_2}{\underset{|}{\overset{OR_1}{\overset{|}{C}}}}-\phi \xrightarrow{h\nu} \phi-\overset{O}{\overset{\|}{C}}\cdot \quad + \quad \cdot\underset{R_2}{\underset{|}{\overset{OR_1}{\overset{|}{C}}}}-\phi \qquad (2)$$

I II

then initiate the subsequent polymerization. It is not clear from the literature which of the radicals I or II is the more likely initiating species. In different reports, it has been stated that the initiating species is the benzoyl radical I [13, 14], the alkoxylbenzyl radical II [15], and both the benzoyl and alkoxylbenzyl radical equally [16]. Clearly, whether photografting occurs depends on the location of the unsaturated grouping in the benzoin derivative and which of the radicals I or II initiates subsequent polymerization. This paper reports the results of some studies with allyl benzoin methyl ether (ABME), and thus it would appear necessary for the alkoxybenzyl radical from ABME to initiate polymerization if it is part of a copolymer onto which it is desired to graft some other monomer.

Although ABME is not an ideal choice because allyl compounds are often difficult to polymerize or copolymerize, it is one of the more readily available unsaturated benzoins. Two possible approaches were examined. (These approaches are the subject of a patent [17].) In the first, ABME was copolymerized with a diallylamine and the resulting copolymer irradiated in the presence of methyl acrylate. In the second, ABME was copolymerized with an acrylic monomer and the resulting copolymer irradiated in the presence of triallylamine.

Copolymers of ABME and Diallylamines

The best yield of an ABME:propyldiallylamine copolymer was only 20% and this required 2.7 mole % of 2,2'-azobisisobutyramidinium dichloride (amido), which was the most effective initiator found; amounts less than 2.7 mole % gave progressively lower yields of polymer. The weight per cent of ABME in the copolymer was usually about one third of the amount in the monomer mixture.

A number of photografting experiments using these ABME: diallylamine copolymers in the presence of methyl acrylate were carried out, but little or no grafting resulted.

Copolymers of ABME and Acrylic Acid (AA)

Copolymers of ABME and AA were readily prepared although only about half of the ABME in the monomer mixture was incorporated into the copolymer.

The results of some experiments on the photochemical behavior

TABLE 2. Photochemical Behavior of an AA:ABME (14% w/w) Copolymer

Crosslinker	Yield of gel after irradiation for 1/2 hr at 360 nm (%)		
	In HCO_2H	In DMF	In EtOH
None	0	< 5	-
Ethylene glycol dimethacrylate (EGDMA)	< 5	10	10
Divinylbenzene (DVB)	-	< 5	-
Triallylamine (TAA)	10	30	30

of an AA:ABME copolymer containing 14 (w/w) % of ABME in the absence and presence of crosslinking monomers are given in Table 2. Irradiation of the copolymer in the absence of a crosslinker very quickly produced a bright yellow solution. On the other hand, the color intensity was very much lower when it was irradiated in the presence of a crosslinker. If the color was caused by the dimerization of two benzoyl radicals to form benzil, the reduced color in the presence of a crosslinker suggests that the benzoyl radicals react preferentially with the crosslinker. Table 2 shows that DMF is the best solvent for the formation of gel. Ethanol was only slightly less effective while formic acid was considerably worse. Ethylene glycol dimethacrylate is a better crosslinker than divinylbenzene under these conditions while triallylamine (TAA) is the best crosslinking monomer.

Table 3 shows that the rate of photografting of TAA to an AA:ABME copolymer depends on the solvent with the rate being greater in ethanol than formic acid. However, the amount of unchanged TAA remained constant as the irradiation time was increased, so that about 33% of TAA monomer was always recovered from the reaction medium. An explanation for this observation could be that the benzoyl radical formed by homolytic fission of ABME initiates the polymerization of TAA to a linear polyTAA, which then grafts in a termination step to the alkoxybenzyl radical which is present as a part of the AA:ABME copolymer. This mechanistic scheme is discussed in greater detail in the following section.

The properties of no-matrix resins prepared by photografting TAA to an AA:ABME copolymer are listed in Table 4. Although the

TABLE 3. Rate of Photografting of TAA onto an AA:ABME Copolymer

Time irradiated at 360 nm (min)	Yield of grafted resin (%)	
	In HCO_2H	In EtOH
10	5	7.3
20	8.7	12
40	14.7	23
80	25	33

TABLE 4. Properties of Some No-Matrix Resins Prepared by Photografting TAA to an AA:ABME Copolymer

	Properties of AA:ABME:TAA resin							
		Amine capacity (meq/g)		Acid capacity (meq/g)		Acid/amine		Thermally regenerable capacity (meq/g)
Solvent	Yield (%)	Analysis	Titration	Analysis	Titration	Analysis	Titration	
HCO_2H	14	2.72	-	7.53	-	2.77	-	0.0
DMF	27	3.29	2.8	6.53	2.8	1.98	1.0	0.0
EtOH	22	2.84	-	6.69	-	2.35	-	0.0

yields of crosslinked resin were low, the amount of amine graft was quite high, which is indicative of the efficiency of benzoin derivatives in initiating the photopolymerization of TAA. The enormous difference between the acid capacity of 6.53 meq/g determined by microanalysis and the acid capacity of 2.8 meq/g determined by titration for one of the resins can be explained as being caused by internal salt structures in which many of the acid and base groups pair up and are then not accessible to the titrant. Table 4 shows that none of the resins had any thermally regenerable capacity, which is the difference between the amount of sodium chloride adsorbed by the resin at 25°C and the amount adsorbed by the resin at 80°C. The absence of any thermally regenerable capacity can again be ascribed to the internal neutralization effect and has been discussed previously [3, 4]. A simple method of reducing the strong interaction between the acid and amine groups in the final resin is to protect either or both acid and amine groups as electrically neutral precursors [4]. Precursors for the acid group include esters, amides, acid chlorides and acid anhydrides. In the following section the acid group was protected as the ester.

Copolymers of ABME and Methyl Acrylate (MA)

Copolymers of ABME and MA were prepared and then were irradiated in the presence of TAA to give polymers which were hydrolyzed to form no-matrix resins. The amine and potential acid sites should be separated, since there is no chance of oppositely charged sites pairing up as in the case with the ABME:AA+TAA system. The crosslinked chains should impose restraints on the movement of the acid groups obtained on hydrolysis and the amine groups and so the resin should have a thermally regenerable capacity.

MA:ABME Copolymers. The properties of some MA:ABME copolymers are listed in Table 5. As the amount of ABME in the monomer mixture was increased, the amount of ABME in the copolymer increased but the amount of ABME in the latter was usually about half of that in the monomer mixture. This is to be expected because of the degradative chain transfer properties

TABLE 5. Preparation of MA:ABME Copolymers

	ABME (% w/w)			
MA:ABME	In monomer mixture	In copolymer	Yield (%)	MW
C1[a]	2.0	-	6	-
C4[b]	2.0	1.35	75	108,000
C5[b]	6.0	3.0	71	100,000
I10[b]	18.0	9.3	68	-
I7[b]	31.0	16.7	68	-
I11[b]	47.0	22.7	54	-

[a] Initiation: 0.5% w/w 2,2'-azobisisobutyronitrile (AIBN).
[b] Initiation: 2.5% w/w AIBN.

TABLE 6. Photografting of TAA onto MA:ABME Copolymer[a]

Solvent	Medium	Yield of resin (%)	Capacity (meq/g)		Acid:base
			Acid	Amine	
Acetone	Solution	10	1.4	4.0	0.35
Benzene	Solution	13	1.4	3.8	0.37
DMF	Solution	17	1.7	3.9	0.43
DMF[b]	Solution	12	2.55	2.8	0.91
DMF	Suspension[c]	58	2.2	3.7	0.6

[a] Irradiated for 90 min at 360 nm.

[b] The ratio of equivalents of acid:equivalents of amine, in the initial reaction mixture was 2.0. In all other experiments the ratio was 1.0.

[c] Suspending medium was paraffin oil.

of allyl compounds and their low copolymerization tendency with MA. This also explains the need to use high concentrations of initiator in order to achieve satisfactory yields (compare C1 and C4).

Photografting of TAA onto MA:ABME Copolymers. In the following discussion the yield and properties of crosslinked or grafted resin refers to the resin after hydrolysis of the ester groups unless stated otherwise.

Table 6 compares the results of some photochemical grafting experiments of TAA onto a MA:ABME copolymer containing 16.7% ABME for polymerizations carried out in solution and under suspension conditions. In solution polymerizations, the best yield was obtained with DMF as solvent. However, better yields were obtained with suspension polymerization, and therefore all subsequent studies were done in suspension systems. One factor contributing to this result is that there is a greater degree of light penetration in the suspension system. Although the ratio of the available acid to amine groups in the reactant solutions for the first three experiments shown in Table 6 was 1.0, it was only between 0.3 and 0.4 in the resulting grafted polymer.

The details for a series of photochemical grafting experiments are listed in Table 7, and the properties of the crosslinked resins after hydrolysis are given in Table 8. An attempt was made in some experiments to determine the fate of all the reactants, and the results of these studies are summarized in Table 9.

TABLE 7. Photochemical Grafting of TAA.HCl onto MA:ABME Copolymer: Polymerization Details

						Composition of suspension							
		Suspending medium				Solvent		MA:ABME			Crosslinker		
Expt. no.	Comments	Type	Vol (ml)	Stirring rate (rpm)	Irradiation time (min)	Type	Vol (ml)	% ABME	g	TAA.HCl (g)	Type	Wt (g)	Solids (%)
L11	EGDMA, 9%	Hexane	60	860	90	DMF	3.7	18	0.81	1.42	EGDMA	0.22	40
L12	Teflon stirrer	Hexane	60	580	90	DMF	3.7	18	0.81	1.42	EGDMA	0.22	40
L13	Paraffin (N_2)	Paraffin	62	113	90	DMF	3.8	18	0.84	1.47	EGDMA	0.22	40
L14	Hexane (N_2)	Hexane	60	670	90	DMF	5.0	18	0.81	1.42	EGDMA	0.22	33
L16		Paraffin	26	550	60	Acetone	1.7	18	1.04	1.84	-		63
L17		Hexane	32	860	60	DMF	2.5	18	1.01	1.78	-		52
L18		Hexane	25	860	60	DMF	2.5	4	0.79	1.5	-		48
L19		Hexane	26	860	60	DMF	2.6	9.3	0.84	1.53	-		48
L20		Hexane	34	760	60	DMF	3.0	22.7	1.1	1.70	-		48
L21	Silylated flask	Paraffin	39	125	60	DMF	2.0	18	0.83	1.46	-		52
L22		Paraffin	23	125	60	Acetone	1.5	18	0.9	1.34^a	-		60
L22C	11% ABME	Paraffin	26	125	60	Acetone	1.7	-	-	1.55^a	-		35
L23		Paraffin	24	125	60	THF	1.8	18	0.96	1.7	-		60
L24	1/4 UV intensity	Paraffin	42	100	60	DMF	2.3	18	0.9	1.58	-		52

L25		Paraffin	42	100	180	DMF	2.3	18	0.9	1.58	-		52
L26	acid/amine = 0.88	Paraffin	57	100	60	DMF	3.0	22.7	1.22	2.0	Hexa-HCl	0.14	53
L27	acid/amine = 0.88	Paraffin	40	100	90	DMF	2.1	22.7	0.85	1.29	Hexa-HCl	0.20	53
L28	acid/amine = 2.0	Paraffin	48	100	90	DMF	2.5	22.7	1.58	1.22	-		53
L29	acid/amine = 3.0	Paraffin	48	100	90	DMF	2.4	19	1.71	0.92	-		53
L30	acid/amine = 2.0	Paraffin	74	150	90	DMF	3.7	19	2.0	1.65	Hexa-HCl EGDMA	0.12 0.66	54
L31C	0.18 g ABME	Paraffin	25	150	90	DMF	1.35		-	1.35[a]	-		53
L32	EA:ABME	Paraffin	102	150	90	i-PrOH	6	19.5	2.02[b]	3.31	-		47

[a] MDAA.HCl.
[b] EA:ABME.

TABLE 8. Photochemical Grafting of TAA.HCl onto MA:ABME Copolymer: Properties of Crosslinked Polymer after Hydrolysis

Expt. no.	Yield (%)	Capacity by titration (meq/g) Acid	Capacity by titration (meq/g) Amine	Acid: amine ratio	Amine capacity from N analysis (meq/g)	Thermally regenerable capacity at pH 6.8 (meq/g)	Comments
L11	53	0.67	2.61	0.25	-	0.0	Very hard, transparent, like NaCl but irregular
L11R	-	3.74	1.48	2.5	2.76	0.08	L11 rehydrolyzed
L12	34	1.06	3.44	0.31	-	0.01	Softer than L11
L13	62	2.78	2.33	1.2	-	-	Similar to L12
L14	42	3.44	1.0	3.4	-	0.35	Heterogeneous
L16	51	2.27	3.17	0.72	4.74	0.21	Almost homogeneous, very soft
L17	44	2.05	3.39	0.60	4.58	0.24	Heterogeneous, harder than L16
L18	21	0.83	4.17	0.20	4.34	-	Heterogeneous, softer than L17
L18R	-	1.28	3.94	0.32	-	-	Rehydrolyzed, very soft
L19	45	1.0	4.0	0.25	4.36	-	Heterogeneous, very soft
L19R	35	2.14	3.42	0.62	-	0.04	Rehydrolyzed

L20	53	0.44	3.89	0.11	3.79	-	
L20R	47	2.42	3.14	0.77	-	0.27	Rehydrolyzed
L21	48	2.0	3.0	0.67	3.95	0.25	Heterogeneous
L22	< 7		0.0		0.0		35% yield homoPMDAA based on amine used
L22C	0						No polymer formed
L23	25	1.11	3.56	0.31	4.07	-	Less heterogeneous than most
L24	18	0.89	3.78	0.23	4.24	-	Less heterogeneous than most
L25	50	2.38	3.56	0.67	4.04	0.23	Heterogeneous
L26	45	2.0	3.44	0.58	4.0	0.29	Heterogeneous, hard
L27	45	0.78	3.11	0.25	3.68	0.25	Hard
L28	45	3.12	2.27	1.37	2.42	0.69	Heterogeneous
L29	13	3.17	2.22	1.43	3.65	0.74	
L30	47	3.23	1.63	1.98	2.92	0.18	Hard
L31C	0						61% yield of polyamine
L32	52	2.23	3.44	0.65	3.8	0.36	

TABLE 9. Photografting of TAA.HCl onto MA:ABME Copolymer: Analysis of the Fate of the Monomers

			Fate of reactants after irradiation (% w/w)					Acid:base ratio in cross-linked polymer		
			Amine			MA:ABME copolymer				
Expt. no.	Acid: base ratio in reactant mixture	Comments	Unchanged monomer	Linear polymer	Cross-linked polymer	Unchanged polymer	Cross-linked polymer	By titration	By microanalysis	Yield of cross-linked polymer (%)
L21	1.0	Silylated	51	0	48	48	47	0.67	0.88	48
L23	1.0	THF	-	-	-	-	-	0.31	0.79	25
L24	1.0	1/4 UV	>65	<12	22	89	11	0.23	0.69	18
L25	1.0	3 hr UV	8	35	54	47	42	0.67	0.81	50
L26	0.88	4% hexa	33	18	49	61	39	0.58	0.77	45
L27	0.88	8.5% hexa	32	23	45	55	45	0.25	1.0	45
L28	2.0		30	27	43	54	46	1.37	2.44	45

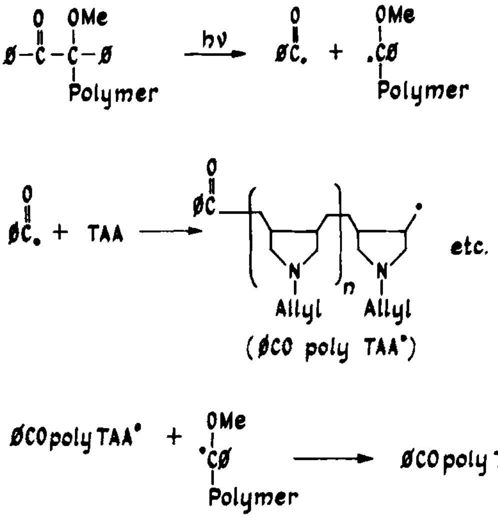
The yield of resin depended on several experimental parameters, one of which was the solids concentration (i.e., total concentration of TAA.HCl plus the MA:ABME copolymer). The best yields of 50 to 60% were obtained by using the most concentrated solutions, while at solids concentrations less than 40% only low yields were obtained. The yield also depended on the suspending medium with paraffin oil being better than hexane. The choice of solvent was also important with DMF being superior to tetrahydrofuran or acetone. The yield was not improved by increasing the irradiation time by a factor of three (L25). Yields were lower when the UV intensity was reduced (L24) and when the acid to base ratio (i.e., the molar ratio of the acid groups to amine groups after hydrolysis of the ester groups) in the reactant solutions was increased (L29). The yield also depended on the amount of ABME in the copolymer and was quite low when less than 9% ABME (L18) was present.

The yields clearly reflect the dependence of the degree and efficiency of crosslinking on the above experimental factors. Thus, an increase in the amount of ABME in the copolymer gives rise to a higher number of grafting and crosslinking points and hence a higher yield. Similarly, high concentrations of TAA favors crosslinking reactions. Although some limited crosslinking may occur via the coupling of two alkoxybenzyl radicals on two different polymer chains, TAA is responsible for the major amount of crosslinking.

Although the yield of crosslinked resin is clearly related to the degree and efficiency of TAA crosslinking, only minor improvements in yield could be achieved by adding additional crosslinkers such as EGDMA and bis-1,6-(N,N-diallylamino)hexane dihydrochloride(hexa-HCl). Tables 8 and 9 show that the addition of EGDMA increases the acid to base ratio and that EGDMA crosslinks only the MA:ABME chains. Similarly, hexa-HCl crosslinks only TAA chains. Thus, the addition of either of these crosslinkers produces a resin richer in either acid or base but the resin is not formed in higher yield. It was thought that the simultaneous addition of the two crosslinkers should improve the yield but again no improvement was found (L30). In these experiments hexa-HCl was more efficiently incorporated into the resin than was EGDMA.

Table 9 shows that resins formed in about 50% yield (L21 and L27) have about 50% of the amine and 50% of the ester which was in the reactant mixture incorporated into the resin. However, resins formed in lower yield (L24) had a higher percentage of amine than was present in the reactant mixture, but the amount of amine in the resin never exceeded 50% of the amount in the monomer mixture. Extending the irradiation time (L25) or adding hexa-HCl (L27) merely resulted in an increase in the amount of linear polyamine formed.

Many of the above observations may be consistent with a sheme [Eqs. (3)] in which the amine polymerization proceeds in two steps with grafting occurring in the termination step. Such a scheme could explain why the yields were always less than 100%. Although there is no direct evidence of grafting and therefore the final resin may be a mixture of two crosslinked resins of the MA:ABME resin and cross-linked TAA, there is some indirect evidence from the results in Tables 8 and 9 that grafting has occurred. For example, photolysis of a MA:ABME copolymer alone gives a very much lower yield of crosslinked product than was obtained when irradiated in the presence of TAA, which therefore acts as an additional crosslinker. It is possible that the crosslinked TAA polymer could merely trap some of the linear MA:ABME copolymer but our experience in the present work suggests that the linear MA:ABME copolymer can be removed by extraction with acetone. In addition, photolysis of a 4% ABME copolymer (L18) in the presence of TAA gave a resin with a lower acid capacity than one obtained by photolysis of a 9% ABME copolymer (L19). This result suggests that a higher concentration of ABME produces a greater concentration of grafting points and hence a larger amount of grafting.



(3)

Resin Properties

The physical appearance of most of the resins was heterogeneous. Resins containing a low degree of crosslinking, such as those prepared using MA:ABME copolymers with less than 9% ABME, were very soft, but strong and hard resins could be obtained by choosing conditions which gave highly crosslinked resins, especially by adding EGDMA, hexa, or both together (L30). Since, as mentioned above, extended irradiation did not increase crosslinking, it therefore did not increase the resin hardness. The size and shape of the resin beads could be controlled by the stirring rate but it had no other effect on the resin properties. The use of a silylated flask and stirrer stopped all sticking of the resin to them during the photopolymerization and often resulted in better shaped beads.

The thermally regenerable capacity for many of the resins are listed in Table 8. The best resins have a thermally regenerable capacity of about 0.7 meq/g (L28 and L29) and an acid:base ratio of 1.4. The ease with which the benzoin derivatives initiate the photopolymerization of TAA leads to resins which have high base capacities (both from titration and microanalysis) and therefore low acid: base ratios. It was therefore often difficult to achieve the optimum acid:base ratio of about 1.4. In some cases, more extensive hydrolysis, such as the use of alcoholic potassium hydroxide, was found necessary in order to achieve complete hydrolysis and the maximum acid:base ratio. A poorly hydrolyzed resin such as L11 had an acid capacity of 0.67 meq/g, an acid:base ratio of 0.25, and no thermally regenerable capacity. Further hydrolysis increased the acid capacity to 3.7 meq/g and the acid:base ratio to 2.5 but only a small improvement in the thermally regenerable capacity was achieved. It thus appears that the acid:base ratio is not the most critical factor in determining the thermally regenerable capacity. A comparison of the acid and thermally regenerable capacities of L11, L11R, L26, and L27 shows that incomplete hydrolysis is unlikely to lower the thermally regenerable capacity. The amount of internal neutralization increased with the degree of hydrolysis so that the amine capacity determined by titration relative to that calculated from microanalysis progressively decreased (compare L11 and L11R).

One important advantage of the photochemical grafting approach to the preparation of no-matrix resins is that the two polymerizations are independent. The light-sensitive benzoin derivative is stable to heat, and therefore the MA:ABME copolymer can be readily formed by using an initiator activated by heat; the grafting of TAA can then be initiated photochemically. Photochemical polymerization of allylamines using benzoin derivatives is one of the best means of carrying out these polymerizations which are not readily initiated by other methods. As the results reported in the tables show, the photografting is rapid, irradiation times of about 60 min being adequate. A disadvantage of the photochemical approach is that soluble polymers are needed in order to obtain sufficient light penetration. A consequence of this could be that the final resin is composed of flexible chains which may then result in unsatisfactorily high degrees of internal neutralization.

EXPERIMENTAL

Materials

The preparation or source of the allylamines, amido, and AIBN have been reported previously [5]. All amines were polymerized as their hydrochlorides. Methyl acrylate (BDH) and acrylic acid were used without removal of inhibitor. ABME was obtained from benzoin, methyl iodide, and allyl chloride as a viscous oil, bp 160-165°C/3 mm [18]. All solvents were of analytical grade.

Instrumentation

UV spectra were recorded on a Beckman DK-2-spectrophotometer or a Unican SP. 800 spectrophotometer. For ABME, λ = 340 nm (ϵ = 204), 342 nm (205), and 338 nm (243) in ethanol, benzene, and methanol, respectively.

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

Titrations for chloride using silver nitrate as titrant were done by use of a Quere Titrator.

All photochemical irradiations of solutions were done in pyrex test tubes at 35°. They were irradiated in a Rayonet photochemical reactor fitted with 16 × 8W lamps, catalog No. R. P. R. 3500 Å, except where otherwise indicated. Some suspension photopolymerizations were carried out with this apparatus but most were irradiated in an Oliphant photochemical reactor fitted with 16 × 8W Sylvania F8T5/BL lamps.

Capacity Measurements

Acid and amine capacities of resins were determined by the following titration procedure. An aliquot of the resin (0.18 g) was shaken for 3-5 days with 0.10 N NaOH (20.0 ml), the slurry centrifuged, and an aliquot (10.0 ml) titrated with 0.10 N HCl. The latter solution was then titrated with 0.05 N $AgNO_3$ solution. From these two titers the acid and amine capacities were calculated.

Thermally regenerable capacities were measured as described previously [2].

Preformed Polymers

PolyTAA. A solution of methyl benzoin methyl ether (0.33 g), anhydrous triallylamine hydrochloride (14 g), and benzene (120 ml) was saturated with nitrogen and irradiated for 1 hr at 360 nm with stirring at 400 rpm. The product was filtered on a sintered funnel, washed with acetone and dried in vacuo to give a white powder (7.3 g, 53%). This sample is referred to as the unwashed sample. The washed sample was obtained by washing on a column successively with 2 N hydrochloric acid, pH 3 hydrochloric acid, acetone, and dried. The weight loss was 11%.

Copolymers of Propyldiallyamine:ABME. A solution of amido (0.42 g, 2.7 mole %), ABME (1.28 g, 12.8 wt %), and methanol (50 ml) was added to anhydrous propyldiallylamine hydrochloride (8.8 g) in a flask which was repeatedly evacuated under vacuum and filled with nitrogen and then heated for 65 hr at 60° C. The solution was cooled and the methanol removed under vacuum and acetone (100 ml) was added and the product obtained, by filtration, as a light pink hygroscopic material which was dried in vacuo to give 1.7 g (17%). The UV spectrum of a sample showed it to contain 4.5% (w/w) ABME, assuming the same absorption properties for ABME in the copolymer as for ABME as the monomer. No polymer was obtained if 1.3 mole % amido was used.

Copolymers of AA:ABME. A solution of AIBN (0.9 g, 4% w/w), AA (14.4 g), ABME (8 g), and ethanol (40 ml) was degassed and heated under nitrogen at 68° C for 18 hr. The clear solution was cooled, diluted with ethanol and poured into excess ether. This purification was repeated and the product dried in vacuo to give 15 g (67%) of polymer which contained 14% (w/w) ABME by UV analysis.

Copolymers of MA:ABME. A solution of MA (11.0 g), ABME (0.22 g), benzene (9 ml), and AIBN (0.3 g, 2.5% w/w) was saturated with nitrogen and heated at 70° C for 20 hr with slow stirring. After cooling, benzene (30 ml) was added and the mixture stirred until all the glassy material had dissolved and the solution poured into hexane (300 ml) with stirring. The purification by precipitation was repeated and the polymer dried in vacuo to give

8.5 g (75%). The sample was found to contain 1.8% (w/w) ABME by UV spectral analysis and had a molecular weight of 120,000 in benzene by viscometry measurement assuming the relationship

$$[\eta] = 2.58 \times 10^{-5}M^{0.85}$$

i.e., there are about 8 ABME units per polymer chain.

Photografting to Preformed Polymers

MA to PolyTAA. A mixture of MBME (0.29 g), benzene (23 ml), unwashed polyTAA hydrochloride (5.8 g), and MA (11.6 g) was stirred under nitrogen for 5 min and then irradiated at 360 nm with stirring under nitrogen for 6 hr. The mixture was diluted with benzene and filtered under suction on a sintered glass funnel and washed successively with benzene and acetone and dried to give polyTAA hydrochloride (5.7 g).

MA to Propyldiallylamine:ABME. The propyldiallyamine hydrochloride:ABME copolymer was irradiated in the presence of MA and several different solvents including methanol and benzene and also additional crosslinkers such as DVB, EGDMA, furan, and diphenyl diacetylene but the maximum yield of crosslinked resin was less than 5%.

TAA to AA:ABME. A solution of an AA:ABME (14% w/w) copolymer (1.2 g) was dissolved in DMF (3.6 ml) by shaking for 12 hr, TAA·HCl (2.4 g) was added and the degassed solution irradiated under nitrogen at 360 nm for 85 min. The crosslinked polymer was isolated by repeated washings with ethanol and finally pH 3 hydrochloric acid and dried in vacuo to give 0.98 g (27%) of resin.

TAA to MA:ABME. The details of the photografting of TAA·HCl onto MA:ABME copolymers are given in Table 7. Resins were isolated by successive washings with hexane, acetone and methanol and then hydrolyzed by heating with 5 N aqueous KOH at 90°C under nitrogen for 24-48 hr, cooled, and washed successively with 0.3 N NaOH, 2 N HCl, and pH 3 HCl and dried in vacuo.

The following is a typical suspension polymerization. A solution of a MA:ABME (19% w/w) copolymer (3.65 g), DMF (6 ml) and anhydrous TAA·HCl (6.48 g) was added to stirred paraffin oil (90 ml) under nitrogen and irradiated at 360 nm for 1 hr with stirring at 550 rpm. The slurry was diluted with hexane and the mixture filtered through a sintered glass funnel and washed and hydrolyzed as described above to give an almost white resin (5.9 g, 58%).

The data for Table 9 were obtained by analyzing the acetone washings for TAA·HCl monomer and unchanged MA:ABME copolymer and the methanol washings for linear polyTAA·HCl.

CONCLUSIONS

AA:ABME and MA:ABME copolymers could be easily prepared and irradiation in the presence of TAA resulted in good grafting. Irradiation, in suspension, of a MA:ABME copolymer gave a resin in about 60% yield with a thermally regenerable capacity of 0.74 meq/g which compares favorably with values of 0.5, 0.9, and 1.2 meq/g for two other no-matrix resins and a plum-pudding resin, respectively [4]. The capacity appears to be limited by rather high degrees of internal salt formation after hydrolysis. Such internal neutralization is probably facilitated by the flexible nature of the acrylic:ABME copolymer chains.

The pendent ally groups in poly TAA were not sufficiently photoactive under the conditions studied to act as grafting locations for the photografting of MA.

PDAA:ABME copolymers could be prepared in only low yields, and irradiation of these copolymers in the presence of MA and several different crosslinkers all failed to yield useful resins.

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