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Grafting of Acrylic Acid and Triallylamine onto Polyacrylamide and Poly-p-isopropylstyrene

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ABSTRACT

Crosslinked polymer beads containing regions of acid and basic groups are the preferred structures for the efficient operation of a thermally regenerable ion-exchange process. The studies reported in this paper were designed to examine the question of grafting between the acidic and basic regions in the resins. Two approaches were used. First, trapped macroradicals from acrylamide were prepared and then either acrylic acid or triallylamine added. The conditions were first optimized for the generation of trapped polyacrylamide macroradicals. Their presence was shown by the grafting of acrylic acid prior to attempted grafting of triallylamine hydrochloride to these macroradicals. The best solvent for the generation of trapped polyacrylamide macroradicals was dioxane. The temperature at which the macroradicals were generated was not very important but grafting to the macroradicals occurred only at elevated temperatures. With acrylic acid up to 25% graft was achieved but the best graft of triallylamine hydrochloride was less than 1%. Secondly, the grafting of triallylamine hydrochloride to an autoxidized polyisopropylstyrene sample containing hydroperoxide groups was attempted. However, no

grafting of triallylamine hydrochloride occurred even though the hydroperoxide groups, in the presence of cobalt naphthenate, initiated rapid and quantitative grafting of acrylic acid.

INTRODUCTION

Thermally regenerable ion-exchange resins must be composed of discrete acidic and basic regions. The problem of the slow rate of salt adsorption by a mixture of conventional-size weak electrolyte acid and base ion-exchange resins may be overcome by the "plum-pudding" concept [1] in which basic and acidic microparticles 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 [2]. 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 [2, 3], and electron micrographs of the resins show them to be composed of discrete acidic and basic domains [3]. It is possible that such resins consist of blocks of grafted acidic and basic chains. One might expect block copolymers to form as a result of the initial formation of a methacrylamide macroradical [3]. 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 [4].

In the first part of this paper conditions were optimized for the grafting of acrylic acid onto trapped polyacrylamide macroradicals and then the grafting of triallylamine hydrochloride onto these macroradicals attempted.

The photografting of triallylamine (TAA) to copolymers of methyl acrylate and allylbenzoin methyl ether (MA:ABME) by using radiation of 360 nm wavelength occurs readily [5]. After hydrolysis, these resins have thermally regenerable capacities which are much lower than the theoretical maximum, and this is attributed to a high degree of internal neutralization which is facilitated by the flexible nature of the MA:ABME copolymer chains [5]. In the photochemical approach, it is difficult to avoid the presence of flexible chains, since uncrosslinked soluble polymers are needed in order to obtain sufficient light penetration during the photografting reaction.

On the other hand, it should be possible to graft to crosslinked polymers with inflexible chains if the polymers have sites which may be activated by heat or a redox reaction. The second part of this paper presents the results of studies made on the introduction of active sites into some soluble polymers as a first step; grafting from these sites was investigated.

RESULTS AND DISCUSSION

Grafting to Trapped Macroradicals

It is possible for a growing polymer chain, under certain conditions, to remain as a trapped macroradical at the completion of the polymerization. The concentration of these trapped radicals may be determined by electron spin resonance measurement [6]. Trapped macroradicals in a polymeric chain offers the possibility of preparing block polymers if another monomer is added under such conditions that the trapped macroradical becomes accessible for further addition [7]. Some of the important parameters governing the formation and reactivity of trapped macroradicals have been determined [8].

The requirements for the successful preparation of block copolymers by the macroradical approach are restrictive, since a number of solubility criteria must be simultaneously satisfied. In addition, the monomer to be grafted should be readily polymerizable. The latter is not the case for allylamines and therefore the conditions were at first optimized for grafting of acrylic acid (AA) onto acrylamide (AAm) macroradicals.

The procedure adopted for the AAm/AA system was to heat the degassed AAm with 2,2'-azobisisobutyronitrile (AIBN) in a solvent for a given time, cool the mixture, and then add degassed AA in a solvent to the precipitated PAAm and heat, usually at a lower temperature than that at which the AAm polymerization was performed.

$$\mathrm{AAm} \xrightarrow[\Delta]{\mathrm{AIBN}} -(\mathrm{AAm})_n- \mathrm{AAm}\cdot \qquad (1)$$

$$-(\mathrm{AAm})_n- \mathrm{AAm}\cdot + \mathrm{AA} \xrightarrow{\Delta} -(\mathrm{AAm})_n-\mathrm{AAm}-(\mathrm{AA})_x- \qquad (2)$$

The w/w% graft was calculated from the expression

$$\text{graft (\% w/w)} = \frac{7.2 \times \text{acid capacity of polymer (meq/g)}}{1 - 0.072\,[\text{acid capacity of polymer (meq/g)}]}$$

Thus, a 100% graft means that the weight of grafted AA is equal to the weight of PAAm to which the AA was grafted. The accuracy of these results depends on how valid several assumptions are. The polymer was washed for several hours with the solvent in which the grafting was carried out (Table 1) and then extracted in a Soxhlet apparatus with hot ethanol for 24 hr, dried, and a sample titrated with 0.10 N NaOH. No further homo PAA could be removed by extraction for longer times with ethanol or by extraction using the solvents shown in Table 1. It was thus assumed that all homo PAA was removed during extraction with ethanol. It was also assumed that the PAAm/PAA copolymer is insoluble in the solvents used to extract PAA. This would be true for copolymers low in PAA but may be less valid if the PAA content is high. Another assumption made was that all copolymer originated from PAAm macroradicals which requires, firstly, that no AAm monomer was left when the AA was added and, secondly, that either all the AIBN had decomposed or that the temperature at which the second stage of the polymerization was performed was such that the rate of decomposition of AIBN was negligible. Tests of these assumptions are discussed below.

The aim was to find the conditions which give the maximum amount of grafting. The results in Table 1 show that the amount of grafting is insensitive to the amount of AIBN initiator in the range 1-5% and to the concentration of the AAm in the precipitating solvent within the range of 9 to 20%. The AA was added as a 30% (v/v) solution in the same solvent. The effect of solvent on the grafting is readily apparent from the data in Table 1. In general, dioxane is the best solvent of those tried, with grafting usually being between 18 and 22%. Similar amounts of grafting were observed with butyric acid but it was less convenient to use and difficult to remove completely from the copolymer. The addition of 2% methylenebisacrylamide (MBAAm) to the AAm to produce a crosslinked macroradical resulted in a reduction of AA grafting from 22% to 19% with a further decrease to 16.5% when 10% MBAAm was used. These results suggest that as the amount of crosslinking agent is increased, more of the macroradicals become sterically inaccessible to the AA.

It seems that some of the macroradicals are destroyed if they are heated too long or heated at too high a temperature. Heating at 73°C for 2 hr (experiments 5, 8-10, 13-15) was found to be the most suitable of the procedures used for the production of the macroradicals. Since the half-life of AIBN, at this temperature, is 2-3 hr, this leaves more than half of it unchanged. Several experiments (e. g., 17, 18) were done in which the macroradicals were washed free of residual

TABLE 1. Block Copolymers of PAAm/PAA from PAAm Macroradicals[a]

No.	Comments	Solvent for generating PAAm macroradicals		Conditions		Yield (%, based on AAm)	Grafting (w/w, %)
		Type	AAm (w/w,%)	For generating macroradicals (°C/hr)	For grafting (°C/hr)		
1		Ethyl acetate	10	73/40	50/65	105	2.4
2		i-PrOH	9	73/40	50/65	100	1.2
3		i-PrOH	20	73/40	50/65	100	1.0
4		i-PrOH	25	79/17	50/65	97	1.5
5		i-PrOH	25	73/2	40/93	83	7
11		EtOH	33	73/2	50/18	95	7
28		nBuOH	12	73/2	48/15	105	11
29		nAmOH	8	73/2	48/15	108	13.5
27		MEK	20	73/2	48/15	100	14.7
30		Glyme	20	73/2	48/15	80	11
33, 40, 37		CH_3CO_2H	12	73/2	48/15	100-110	3.5-5
38		$CH_3CH_2CH_2CO_2H$	12	73/2	48/15	130	25
8-10, 13-15	AIBN 1-5%	Dioxane	9-20	73/2	48/15	90-130	18-22
16		Dioxane	20	79/16	50/19	115	10
17, 18	Purified macroradical	Dioxane	20	73/2	50/19	102	12

(continued)

TABLE 1 (continued)

No.	Comments	Solvent for generating PAAm macroradicals: Type	Solvent for generating PAAm macroradicals: AAm (w/w, %)	Conditions: For generating macroradicals (°C/hr)	Conditions: For grafting (°C/hr)	Yield (%, based on AAm)	Grafting (w/w, %)
31	2% MBAAm	Dioxane	12	73/2	50/19	130	19
32	10% MBAAm	Dioxane	12	73/2	50/19	127	16.5
19, 20		Dioxane	20	73/2	RT/44	55	0.5
Formation of macroradicals by UV irradiation							
23	tBuOOH	Dioxane	20	UV/2	50/19	91	17.6
26	$(C_6H_5)_2CO$	Dioxane	20	UV/$1\frac{1}{4}$	50/19	77	11
34, 35	$(C_6H_5)_2CO$	CH_3CO_2H	12	UV/2	50/19	30	2

[a]Molar ratio of AA:AAm = 2:1.

AIBN with solvent under an atmosphere of nitrogen before adding the AA. Under these conditions a reduced, but still significant amount of grafting occurred proving that macroradicals were present and that they initiate the grafting of AA. The reduction in the percent grafting could be an indication that residual AIBN and residual AAm are partly responsible for the production of the copolymer but the macroradical concentration could also have been reduced by reaction with traces of oxygen inadvertently introduced during the washing procedure.

Only 0.5% grafting occurred when AA was added to the macroradical and the system kept at room temperature for 44 hr (Expts 19, 20). Thus heating is required for the second stage as well as the first. This fact may be explained if it is assumed that uncoiling of the macroradical is required before it can react further with AA. Some uncoiling will be facilitated by the appropriate choice of solvent (and monomer if some alternative to AA were being considered) but apparently further uncoiling caused by heating is required. The uncoiling and corresponding increase in reactivity of the macroradicals explains why their yield is reduced in experiments at higher temperatures. These observations suggest that rather than to prepare the macroradical at 73°C and to carry out the grafting at 50°C, it would be better to prepare the macroradical at lower temperature where the yield should be greater because of the reduced reactivity of the macroradical due to greater coiling; the grafting would then be carried out at an elevated temperature. Attempts to prepare PAAm macroradicals at room temperature by use of redox initiators such as tert-butyl hydroperoxide/dimethylaniline were unsuccessful, and therefore a photochemical approach was used.

In a control experiment, AAm in dioxane was irradiated with 360 nm wavelength radiation at room temperature in the presence of tert-butyl hydroperoxide for 2 hr, the radiation turned off, and the mixture heated at 50°C for 19 hr to give a 92% yield of PAAm. When AA was added to the PAAm macroradical before heating at 50°C for 19 hr a 91% yield of copolymer was obtained with 17.6% grafting. Since the formation of copolymer could have been initiated by residual tert-butyl hydroperoxide, further UV studies were performed in which the only source of radicals for grafting was the macroradicals formed during UV irradiation.

In another control experiment, AAm in dioxane was irradiated with 360 nm wavelength radiation at room temperature in the presence of benzophenone for 75 min, the radiation turned off, and the mixture heated at 50°C for 17 hr to give a 72% yield of PAAm. When AA was added to the macroradical which had been generated photochemically, a 77% yield of copolymer with 11% grafting was obtained. Thus, block copolymers are formed when AA is added to PAAm macroradicals generated photochemically. However, the expectation that a greater concentration of macroradicals would be produced at lower

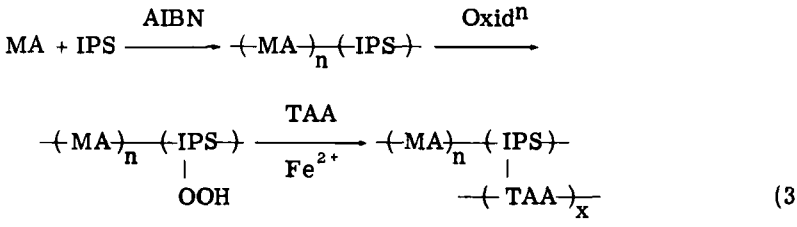
temperatures and that these would give rise to a greater amount of grafting at elevated temperatures was not realized.

Dioxane was the best solvent of those tried for the generation of PAAm macroradicals and no advantage was gained by generating them at low temperatures.

Several attempts were made to graft di- and triallylamine hydrochlorides to PAAm macroradicals but the best degree of grafting was only 0.5%. Unfortunately, the allylamine hydrochlorides were insoluble in dioxane. Methyl ethyl ketone (MEK) was the best solvent which both dissolved the amine hydrochlorides and led to reasonable grafts of AA onto PAAm macroradicals. However, negligible grafts of methyldiallylamine hydrochloride or triallylamine hydrochloride onto PAAm macroradicals in MEK were obtained.

Grafting to Peroxidized Polymers

An approach in which hydroperoxide groups are introduced as grafting sites into copolymers of methyl acrylate (MA) and p-isopropylstyrene (IPS) may be summarized as in Eq. (3).



(3)

Although the oxidation and especially the autoxidation of cumene has been extensively studied [9] and methods have been found for obtaining hydroperoxide, the peroxidation of polystyrene (PS) proceeds only with great difficulty to give low yields of hydroperoxide, whereas polyisopropylstyrene (PIPS) is peroxidized more readily [10-12].

A number of oxidations of PIPS were performed under different conditions with the aim of maximizing the yield of hydroperoxide. The results are listed in Table 2 and show that more peroxidation of PIPS occurs in solution than when an emulsion system is used and that peroxide-forming solvents such as dioxane and cumene are better solvents than benzene. However, extremely long oxidation times are needed in order to achieve 20% hydroperoxide content. This appears to be a maximum value and may be explained by assuming that the rate of formation of new hydroperoxide groups is equal to that rate of decomposition of the groups already present. For a satisfactory

TABLE 2. Autoxidation of PIPS

No.	Conditions	Hydroperoxide (%)
41	Emulsion of PIPS in cumene in H_2O, Na_2CO_3, K stearate oxidized by bubbling oxygen through it at 80°C for 24 hr	1.5
42	Oxygen bubbled through solution of PIPS in cumene at 80°C in presence of benzoyl peroxide	
	5 hr	1.97
	24 hr	6
	120 hr	21
43	Oxygen bubbled through solution of PIPS in dioxane at 80°C in the presence of benzoyl peroxide	
	0 hr	0.6
	88 hr	15
	112 hr	15
44	Oxygen bubbled through solution of PIPS in benzene at 80°C in the presence of benzoyl peroxide	
	0 hr	0.6
	88 hr	3.7

ion-exchange resin, the final copolymer of, for example, MA and IPS should contain less than 10% of IPS, in order that it have a sufficiently high acid capacity (after hydrolysis), and since only 20% of the IPS groups present can be oxidized, the concentration of grafting sites for grafting triallylamine will be very low. Hence, before grafting to hydroperoxidized copolymers of MA and IPS was attempted, grafting to hydroperoxidized PIPS was studied.

The results of the attempted grafting of AA and triallylamine hydrochloride (TAA·HCl) to a PIPS containing 17% hydroperoxide residues are shown in Table 3.

Acrylic acid reacted violently in the presence of a peroxidized PIPS sample and cobalt naphthenate to give an almost quantitative graft. On the other hand, no grafting or homopolymerization of TAA·HCl occurred under similar conditions. Unless a higher concentration of hydroperoxide can be introduced into PIPS at a faster rate than that found in this study, chemical grafting does not seem practicable. Even if higher concentrations of hydroperoxide could

TABLE 3. Grafting to PIPS (17% Hydroperoxidized)

No.	Conditions	Portion of monomer which grafted (wt %)[a]
45	AA added to a solution of PIPS in benzene under nitrogen and then Co naphthenate added	100
46	As for 45 but with TAA·HCl instead of AA	0
47	As for 46 but with MEK instead of benzene	0
48	Redox system with $FeSO_4$ and TAA·HCl	0

[a]Ratio of weight of AA or TAA·HCl to the weight of PIPS (17% hydroperoxidized) was 5.2.

be produced, the insensitivity of TAA·HCl to this initiation system would limit copolymer formation.

EXPERIMENTAL

Materials and Instrumentation

AIBN (Fluka, purum), benzophenone (BDH), tert-butyl hydroperoxide (75% + 25% tert-butyl peroxide, La Porte), acrylamide (Merck), methylenebisacrylamide (Fluka, pract.) and acrylic acid were used without purification. All solvents were of analytical reagent grade. Peroxides were removed from glyme, dioxane and MEK immediately before use by passing them through an alumina column.

Ultraviolet irradiation experiments were done by using an Oliphant photochemical reactor fitted with 16 × 8W Sylvania F8T5/BL lamps.

Extraction of Polyacrylic Acid

The conditions used for the generation and the reaction of macroradicals are summarized in Table 1. The grafted resin was extracted for several hours with the hot solvent in which the grafting was performed and then extracted in a Soxhlet with ethanol for 24 hr.

Preparation and Polymerization of p-Isopropylstyrene (IPS)

IPS was prepared from cumaldehyde and methylmagnesium iodide [13]. This procedure yielded p-isopropyl-α-hydroxyethylbenzene rather than the claimed IPS [13], which was obtained by dehydration of the p-isopropyl-α-hydroxyethylbenzene by shaking at room temperature for several minutes with 50% sulfuric acid and extraction into ether.

A solution of IPS (4.6 g) and AIBN (0.05 g) in benzene (5 ml) was degassed with nitrogen and heated at 70°C for 20 hr, cooled, and poured into methanol. The precipitate was dissolved in benzene and the polymer again precipitated with methanol to yield 3.2 g (70%) of PIPS.

The conditions used for the autoxidation of PIPS and the grafting to autoxidized PIPS are summarized in Tables 2 and 3, respectively.

The hydroperoxide content of the autoxidized PIPS samples was determined by a modified iodometric titration [14]. The hydroperoxide content expressed as a percentage of the theoretical maximum was calculated from the expression:

$$\% \text{ hydroperoxide} = \frac{(T_2 - T_1) \times 0.10 \times E \times 100}{2w}$$

where T_2 = 0.10 M $Na_2S_2O_3$ titer for a weight w of sample (mg), T_1 = 0.10 M $Na_2S_2O_3$ titer for a blank titration, and E = equivalent weight of hydroperoxide = 179 for PIPS hydroperoxide.

CONCLUSIONS

Although AA grafts readily to trapped PAAm macroradicals and to hydroperoxidized PIPS, no conditions were found under which TAA·HCl grafted to trapped PAAm macroradicals or under which TAA·HCl grafted to hydroperoxidized PIPS.

REFERENCES

[1] H. A. J. Battaerd, N. V. Blesing, B. A. Bolto, A. F. G. Cope, G. K. Stephens, D. E. Weiss, D. Willis, and J. C. Worboys, Effluent Water Treatment J., 14, 245 (1974).

[2] B. A. Bolto and R. V. Siudak, J. Polym. Sci. Polym. Symp. Ed., 55, 87 (1976).
[3] B. A. Bolto, M. B. Jackson, R. V. Siudak, H. A. J. Battaerd, and P. G. S. Shah, J. Polym. Sci. Polym. Symp. Ed., 55, 95 (1976).
[4] M. B. Jackson, J. Macromol. Sci.–Chem., A10, 959 (1976).
[5] M. B. Jackson and W. H. F. Sasse, J. Macromol. Sci.–Chem., A11, 1137 (1977).
[6] C. H. Bamford, A. D. Jenkins, D. J. E. Ingram, and M. G. R. Symons, Nature, 175, 894 (1955).
[7] C. H. Bamford and A. D. Jenkins, Proc. Roy. Soc. (London), A216, 515 (1953).
[8] R. B. Seymour, P. D. Kincaid, and D. R. Owen, Adv. Chem. Ser., 129, 230 (1973).
[9] R. K. Srivastava and R. D. Srivastava, J.Catal., 39, 317 (1975).
[10] W. Hahm and L. Lechtenbohmer, Makromol. Chem., 16, 50 (1955).
[11] D. J. Metz and R. B. Mesrobian, J. Polym. Sci., 16, 345 (1955).
[12] J. D. Matlack, S. N. Chinai, R. A. Guzzi, and D. W. Levi, J. Polym. Sci., 49, 533 (1961).
[13] A. Klages and R. Keil, Ber., 2, 1632 (1903).
[14] N. D. Cheronis and T. S. Ma, Organic Functional Group Analysis, Interscience, New York, 1964, pp. 206, 529.

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