Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Reaction of Thiols and Bisulfite with the Pendant Allyl Groups in Polytriallylamine

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To cite this Article Eppinger, K. H. and Jackson, M. B.(1980) 'Reaction of Thiols and Bisulfite with the Pendant Allyl Groups in Polytriallylamine', Journal of Macromolecular Science, Part A, 14: 1, 121 — 136

To link to this Article: DOI: 10.1080/00222338008063213
URL: http://dx.doi.org/10.1080/00222338008063213

J. MACROMOL. SCI.–CHEM., A14(1), pp. 121-136 (1980)

Reaction of Thiols and Bisulfite with the Pendant Allyl Groups in Polytriallylamine

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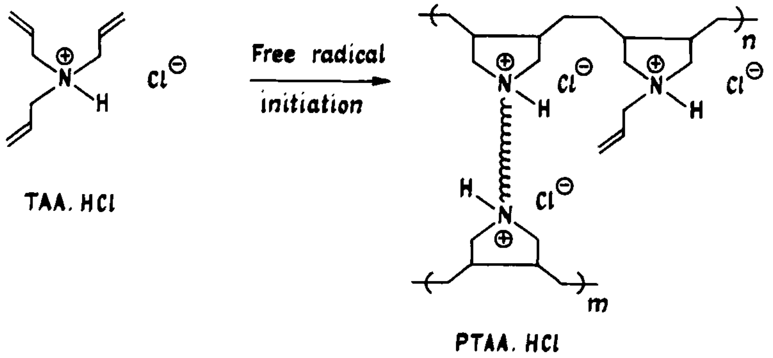
ABSTRACT

The infrared spectrum of polytriallylamine prepared by the free-radical-initiated polymerization of triallylamine indicates the presence of a substantial amount of unsaturation. The usual quantitative methods of determining unsaturation (e. g., bromide/bromate and mercuric acetate) cannot be used on polytriallylamine because of interference from the amino group. On the other hand, bisulfite was found to react rapidly and quantitatively with the pendant allyl groups of polytriallylamine. The reaction was studied over the pH range 4 to 10 and was fastest at pH 5.2. The reaction is a free-radical reaction which is catalyzed by metal ions and oxygen. The sulfonic acid groups which result from attack of bisulfite on the pendant allyl groups of polytriallylamine form strong zwitterion structures with the amine nitrogens. The addition of thiols is also a free-radical reaction. The reaction of $HSCH_2CH_2OH$, $HSCH_2CO_2H$, CH_3SH, H_2S, $HSCH_2CH_2N(C_2H_5)_2$, CH_3COSH, and C_6H_5SH with polytriallylamine was studied. Of these compounds, only $HSCH_2CH_2OH$ and $HSCH_2CO_2H$ reacted quantitatively. Some reasons for the differences in reactivity are presented.

INTRODUCTION

The cyclopolymerization [1] of triallylamine gives polymers containing mainly five-membered ring structures [2] with the pendant allyl group giving rise to crosslinking [Eq. (1)]. However, the



(1)

infrared spectrum (Fig. 1a) of such polymers shows them always to contain some unsaturation because not all the pendant allyl groups react in the crosslinking step. This paper is concerned with determining the degree of unsaturation in polytriallylamine (PTAA) and reports the results of a study of the reactivity of the pendant allyl groups with bisulfite and with thiols.

RESULTS AND DISCUSSION

Reaction of Bisulfite with PTAA

Infrared spectra (Fig. 1b) shows that all unsaturation in PTAA is removed by reaction with bisulfite, and the reaction is rapid and quantitative at pH 5 (Fig. 2). This is in contrast to many bisulfite additions to simple olefins where free-radical initiators, heat and pressure [3, 4], ultraviolet radiation [5], and γ irradiation [6] are needed.

The percent sulfur in PTAA samples after complete reaction with bisulfite provides a convenient means of measuring the degree of unsaturation and hence the amount of crosslinking in a PTAA sample. Table 1 shows that PTAA samples prepared with different initiators have different degrees of unsaturation. PTAA prepared by using irradiation from a ^{60}Co source was the most saturated and most highly crosslinked polymer but polymers prepared using different redox initiation systems had different amounts of unsaturation which

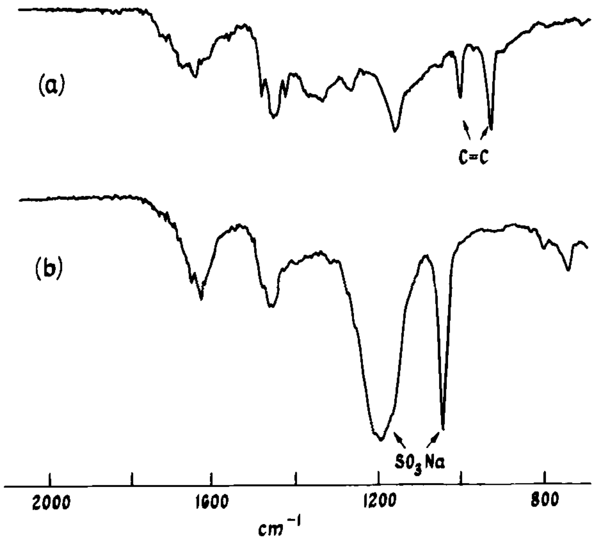


FIG. 1. Infrared spectra of PTAA (as free base form): (a) before reaction with bisulfite; (b) after reaction with bisulfite.

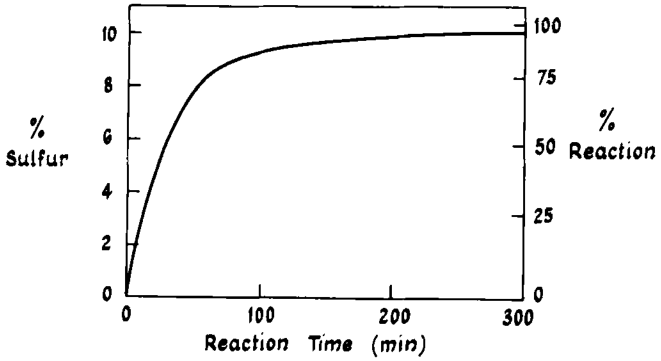


FIG. 2. Rate of reaction of bisulfite with PTAA. Samples of resin were shaken with an excess of a 0.2 M NaHSO$_3$ solution at pH 5.0, washed, dried, and analyzed for sulfur. The infrared spectrum of a sample containing 10.3% sulfur showed the absence of unsaturation.

TABLE 1. Reaction of Bisulfite with PTAA Made by Different Methods

Mode of initiation used to polymerize TAA	S (%)	Base capacity (meq/g)[a]
Radiation (Co^{60} source)	7.2	3.2
Ti^{3+}/H_2O_2	9.1	2.15
Fe^{2+}/H_2O_2	10.3	1.55
Fe^{2+}/t-BuOOH	10.8	1.3

[a] After shaking with 10-fold excess of 0.2 M $NaHSO_3$ for 24 hr at pH 5.2. The S content and base capacity were measured on the polymer in the free base form.

depended on the initiator used. Except where indicated otherwise, all other results reported in this paper were obtained from studies on PTAA samples made by using the Fe^{2+}/H_2O_2 redox system.

PTAA containing 10.3% S corresponds to the composition $(PTAA)_{1.7}(SO_3H)$, i. e., if bisulfite has reacted with all the double bonds, there is one double bond per 1.7 nitrogen atoms in the cross-linked resin before bisulfite reaction. Reaction with bisulfite reduced the experimentally determined base capacity from 6.9 meq/g (theoretical value is 7.3 meq/g for the PTAA) to 1.55 meq/g after treatment. About half this capacity loss can be attributed to the presence of the sulfonate group as a diluent, and the other half to internal salt formation between sulfonate and ammonium groups. Although there have been two reports of the formation of disulfonates [3, 7] it has been assumed on steric grounds that only one sulfonate group can add to each allyl group of PTAA, as shown in Eq. (2).

$$>NCH_2CH{=}CH_2 + HSO_3^- \longrightarrow >NCH_2CH_2CH_2SO_3^- \qquad (2)$$

The free-radical mechanism shown in Eqs. (3)-(5) for the addition of bisulfite to olefins to give anti-Markownikoff products has been proposed [8]:

Initiation:

$$SO_3^{2-} + \text{oxidant} \longrightarrow {}^{\bullet}SO_3^- + \text{oxidant}^- \qquad (3)$$

Addition:

$${}^{\bullet}SO_3^- + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2SO_3^- \qquad (4)$$

TABLE 2. Effect of Inhibitors on the Reaction of Bisulfite with PTAA[a]

pH	Inhibitor	Concentration (M)	S (%)	Base capacity (meq/g)
7.2	None	–	6.15	3.5
	EDTA[b]	9×10^{-3}	2.6	5.2
	Hydroquinone	1.8×10^{-2}	2.5	5.6
	Hydroquinone	0.45×10^{-2}	3.5	4.8
5.2	None	–	9.5	2.1
	EDTA	9×10^{-3}	7.9	2.8
	EDTA	2.3×10^{-3}	7.8	2.9
	Hydroquinone	1.8×10^{-2}	7.5	2.8
	Hydroquinone	0.45×10^{-2}	8.7	2.4

[a] $[HSO_3^-]_0 = 0.10$ M, equivalents of bisulfite/equivalents of nitrogen in the polymer = 3.5, samples shaken for 18 hr in aqueous solutions saturated with nitrogen.

[b] EDTA = ethylenediaminetetraacetic acid, disodium salt.

Chain transfer:

$$R^{\bullet}CHCH_2SO_3^- + HSO_3^- \longrightarrow RCH_2CH_2SO_3^- + {}^{\bullet}SO_3^- \qquad (5)$$

It has recently been shown [5] that the sulfite radical ion is the main chain carrier at pH 5 and the hydrogen sulfite radical at pH 3. No studies of the reaction of bisulfite with unsaturated crosslinked polymers have been reported.

The reaction of the model compound, allylamine hydrochloride, with sodium bisulfite gave a product, which after freeze-drying showed no methyl group in the nuclear magnetic resonance spectrum. This indicates an anti-Markownikoff addition of bisulfite to allylamine.

The results in Table 2 indicate that the addition of bisulfite to PTAA is a free-radical reaction. Reaction is inhibited by both hydroquinone and EDTA; the latter indicating that trace amounts of metals catalyze the reaction. There is less inhibition at pH 5.2 than at pH 7.2 but it is still apparent, probably because this is the optimum pH for the addition reaction (Table 3). Reported pH optima range from pH 5 to 9 for the addition of bisulfite to simple olefins [3]. The optimum pH of 5.2 for the addition to PTAA is near where the

TABLE 3. Effect of pH on the Addition of Bisulfite to PTAA[a]

pH	S (%)	Base capacity (meq/g)
4.2	7.2	3.0
5.2	9.5	2.1
6.2	7.3	3.1
7.2	6.15	3.5
8.2	2.4	5.8
9.2	1.5	6.2
10.2	1.0	6.4

[a] $[HSO_3^-]_0$ = 0.10 M, equivalents of bisulfite/equivalents of nitrogen in the polymer = 3.5, samples shaken for 18 hr in aqueous solution saturated with nitrogen.

concentration of free bisulfite ions is maximum [9], even though at this pH and above, the most likely chain carrier is the sulfite radical ion rather than the bisulfite radical [5]. The decreased reaction at pH 4.2 may be explained by assuming that the bisulfite radical is also involved at this pH and that it is less reactive. The approach of the negatively charged sulfite radical ion to the positively charged resin would be expected to be favored over the approach of the neutral bisulfite radical. Another contributing factor to the reaction of PTAA with bisulfite is the degree of ionization of the polymer. At pH values less than 6 the polymer is almost completely protonated and therefore is more hydrophilic and more swollen in water than at higher pH. It should therefore be more accessible to the bisulfite reagent.

Table 4 indicates that the rate of the reaction with PTAA is only slightly increased by the presence of oxygen. However, it is not possible to give a quantitative measure of this effect in unbuffered solutions since the accompanying oxidation of bisulfite to bisulfate resulted in a large decrease in pH. Even in buffered solutions, considerable change in pH was observed when oxygen was bubbled through the solutions. Furthermore, the extent of reaction depended on the nature of the buffer and therefore detailed studies of the effect of oxygen at constant pH were not made.

All the bisulfite addition reactions reported in Tables 1-4 were done at 20°C. No difference in the extent of reaction was observed when the reactions at pH 6.2 and 7.2 (Table 3) were carried out at 80°C. A free-radical reaction would be expected to be almost independent of temperature.

TABLE 4. Effect of Oxygen on the Addition of Bisulfite to PTAA[a]

		pH		
Buffer	Atmosphere	Initial	Final	S (%)
None	Nitrogen	7.2	7.2	6.15
None	Air[b]	7.2	7.2	6.8
None	Oxygen[c]	7.2	4.0	9.4
Phosphate	Nitrogen	7.2	7.2	4.0
Phosphate	Air[b]	7.2	7.2	4.8
Phosphate	Air[d]	7.2	5.0	8.9
Phosphate	Oxygen[c]	7.2	4.7	7.0

[a] $[HSO_3^-]_0$ = 0.10 M, equivalents of bisulfite/equivalents of nitrogen in the polymer = 3.5, samples shaken for 18-24 hr.

[b] Initially exposed to air and then sealed.

[c] Oxygen bubbled through the solution during the reaction.

[d] Air bubbled through the solution during the reaction.

A study of the effect of initial bisulfite concentration on the reaction with PTAA was hampered by experimental difficulties. All the experiments were so designed that the ratio of equivalents of bisulfite to equivalents of nitrogen in the resin was a constant value. Thus at low bisulfite concentrations large volumes of solution had to be filtered from small amounts of resin. The filtration of such large volumes took a long time thus increasing the chance of small amounts of air being inadvertently admitted to the solution and the addition of air would then increase the rate of addition of bisulfite. Table 5 shows that the percent sulfur in the resin after shaking for 24 hr increased as the initial concentration of bisulfite decreased. This trend was reproducible. After shaking for 11 days the percent sulfur in each of the resins was similar. Since the initial rate of bisulfite addition was found to be proportional to $[\text{bisulfite}]^{1/2}$, it follows that as the reaction proceeds the rate must decrease and, further, the rate at which it decreases must be greater for the more concentrated bisulfite solutions. One possible explanation for these results is as follows. In concentrated bisulfite solutions the initial rate of reaction is faster than in more dilute solutions. Since it is faster it reacts very quickly with the more exposed double bonds and the sulfonate groups so formed then reduce the rate of migration of further bisulfite into the resin. At lower bisulfite concentrations, the slower initial reaction means that a more even distribution of the bisulfite may be achieved before reaction occurs.

TABLE 5. Effect of Concentration on the Addition of Bisulfite to PTAA[a]

	S (%)	
[HSO_3^-] (M)	After 1 day	After 11 days
0.10	5.4	7.9
0.010	6.8	7.4
0.0025	7.0	7.3

[a] Equivalents of bisulfite/equivalents of nitrogen in the polymer was 1.39 in each case, pH 7.2, solutions saturated with nitrogen, polymers isolated by washing with nitrogen-saturated 0.3 N NaOH under nitrogen.

About half of the base capacity loss of PTAA resulting from reaction with bisulfite is attributable to the presence of the sulfonate group as a diluent and the other half to internal salt formation between the sulfonate and the ammonium groups. Further information on the nature and strength of these internal salt structures can be obtained by measuring the acid and base capacity of the bisulfite treated polymer in the acid and base form. The optimum pH for the reaction is 5.2, and at this pH PTAA is completely in the protonated form (I) (Fig. 3). Treatment with bisulfite should give the product II, but if the tendency for salt formation is very great, product III may form. The polymer is usually then converted to the free base form by washing with 0.3 N NaOH to give product IV. Subsequent washing with water until the washings are neutral results in the formation of V. Microanalysis of V shows that it is free of chloride and sodium. Furthermore, in a control experiment, a slurry of PTAA (in the free base form, pH 7.0) was mixed with a solution of the bisulfite adduct of benzaldehyde (pH 6) and the pH immediately increased to 9.7. This indicates that a salt is formed with the liberation of sodium hydroxide. In an alternative work-up procedure, product II is washed successively with 2 N HCl and then pH 3 HCl. These washings could either leave II unchanged, could convert II to product VI or convert II to product VII. Product VII is confirmed by microanalysis which shows no sodium and a chloride value equal to (total milliequivalents nitrogen minus milliequivalents sulfonic acid group). There are therefore two possible structures, V and VII which depend on whether the polymer was worked up by alkali or acid and both contain strong internal salt structures.

The product V was shaken with excess 0.1 N HCl and back-titrated to give a base capacity of 2.0 meq/g. Product V was also shaken

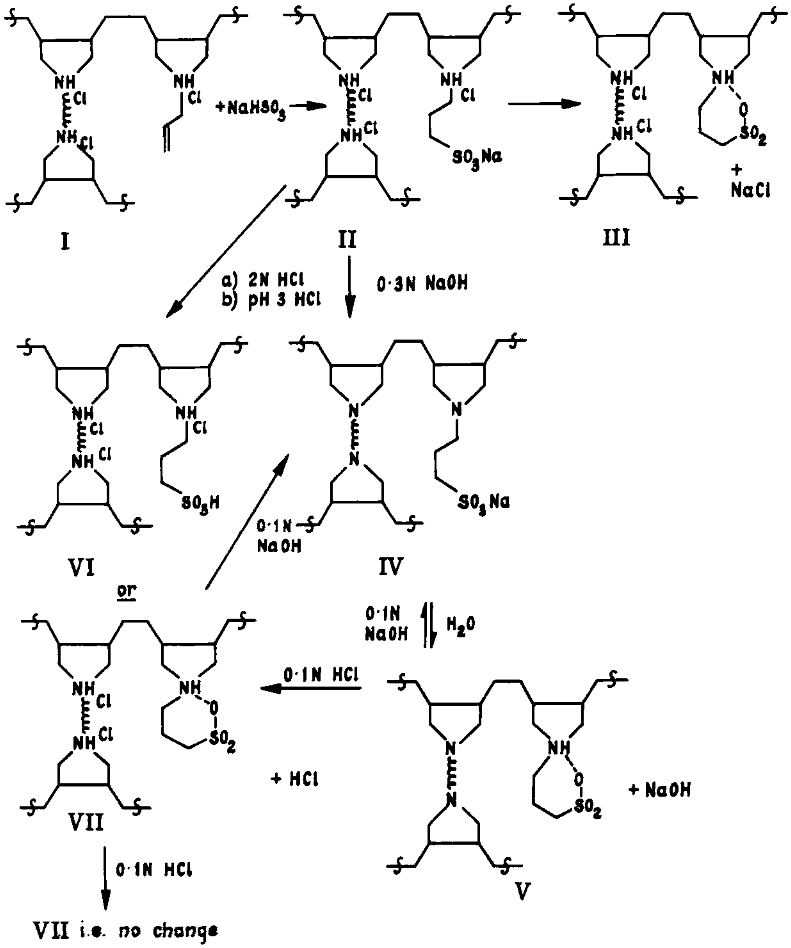


FIG. 3. Scheme for reaction of bisulfite with PTAA.

with 0.1 N NaOH and back-titrated to give a NH. . . SO_3 capacity of 2.5 meq/g.

Product VII was shaken with excess 0.1 N HCl and back-titrated to give a base capacity of 0.0 meq/g and also shaken with 0.1 N NaOH and back-titrated to give a total acid capacity of 4.2 meq/g. From a titration of the liberated chloride with $AgNO_3$ the NHCl capacity was found to be 1.95 meq/g and therefore the NH. . . SO_3 capacity is 2.25 meq/g. Table 6 summarizes these results. Thus, the internal salt structure is not broken by 0.1 N HCl but it is broken by 0.1 N NaOH. As soon as the alkali is diluted or replaced by water the internal salt structures reform.

TABLE 6. Acid and Base Capacities for Polymers of Structures V and VII

Starting polymer	Treatment	Product	Free N (meq/g)	NH. . . SO_3 (meq/g)	NHCl (meq/g)
V	0.1 N HCl	III	2.0[a]		
V	-	V	2.5[b]	3.0[b]	
V	0.1 N NaOH	IV		2.5[a]	
VII	0.1 N HCl	VII[c]			
VII	-	VII		2.73[b]	2.33[b]
VII	0.1 N NaOH	IV		2.25[a]	1.95[a]

[a] Measured.
[b] Theoretical values.
[c] No acid uptake.

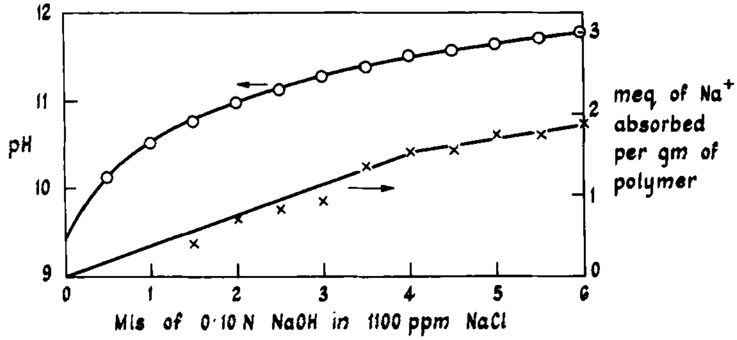


FIG. 4. Titration curve for polymer of structure V with (○) 0.1 N NaOH and (×) its Na^+ uptake (0.16 g of polymer was shaken with 20 ml of solution for each point). Na^+ uptake was measured by atomic absorption spectroscopy.

Figure 4 shows the titration curve for the free base polymer of structure V. There is no clear endpoint, but if the endpoint is taken as 4 ml (pH = 11.5) an NH. . .SO_3 capacity of 2.5 meq/g is found (compare Table 6) and a $pH_{1/2}$ of 11. The latter value indicates the strength of the internal salt structure. Figure 4 also shows that sodium is adsorbed by the polymer. The amount of sodium adsorbed by the polymer in the presence of 4 ml of 0.1 N NaOH corresponds to 1.6 meq/g.

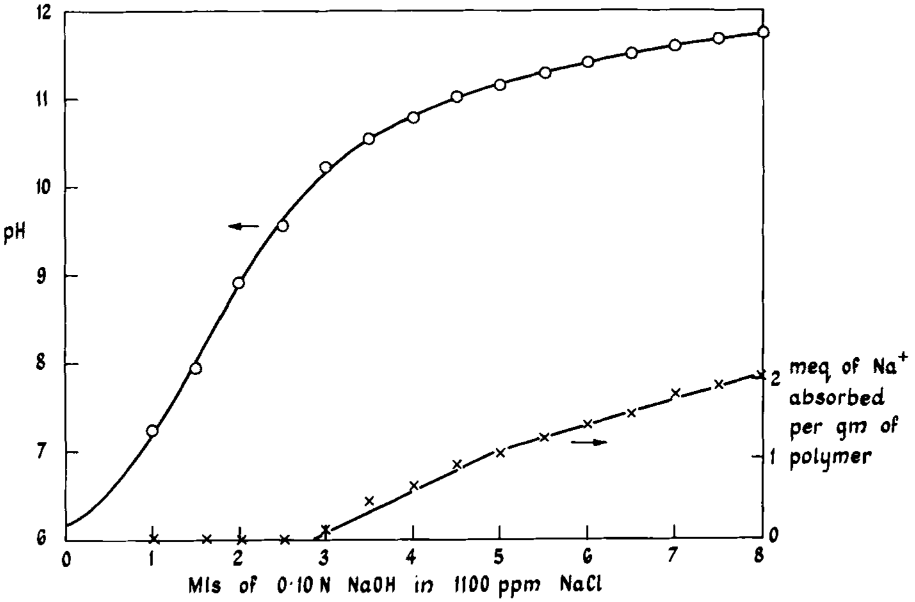


FIG. 5. Titration curve for polymer of structure VII with (○) 0.1 N NaOH and (×) its Na^+ uptake (0.16 g of polymer was shaken with 20 ml of solution for each point). Na^+ uptake was measured by atomic absorption spectroscopy.

Figure 5 shows the titration curve for the HCl salt of the polymer of structure VII. Again, no clear endpoints are apparent, but a value of 3.15 ml corresponds to a capacity of 1.95 meq/g (compare Table 6) which represents the titration of the NHCl groups. From this curve the $pH_{1/2}$ for such groups is 7.95, which is somewhat higher than that for the nonsulfonated PTAA. A second endpoint at 6.75 ml (pH 11.5) then corresponds to a total acid capacity of 4.2 meq/g and the latter portion to titration of the NH. . .SO_3 group. These assignments are confirmed by the sodium uptake of the resin. No sodium was adsorbed by the polymer until all of the NHCl groups had been neutralized after which the polymer adsorbed sodium at a rate such that in the presence of 6.75 ml of NaOH the amount of sodium adsorbed corresponded to about 1.6 meq/g.

Reaction of Thiols with PTAA

Thiols react with olefins by a free-radical mechanism to give anti-Markownikoff products [4, 10]. Thiols have been used to cure polymers [11, 12], and thiols react with polybutadiene [13], but reactions with crosslinked polymers have not been reported.

TABLE 7. Reaction of Some Thiols with PTAA[a]

Expt.	Sulfur compound	Ratio of equivalents sulfur compound to equivalents N in PTAA	Concn of sulfur compound (M)	Solvent	Initiator	Reaction time (days)	Reaction (%)[b]
M14	Thiophenol	1.0	0.65	MeOH	Air	4	0
M15	Thiophenol	1.0	0.65	DMF	Air	4	0
M18	Thiophenol	1.5	1.0	MeOH	BO/DMA[c]	0.67	0
M22	Thioacetic acid	1.0	0.8	H_2O	H_2O_2/Fe^{2+}	3	0
M23	H_2S	4.0	0.1	H_2O	UV/ acetone	0.75	0
M24	H_2S	1.6	0.1	H_2O	H_2O_2/Fe^{2+}	3	18
M21	Methanethiol	2.0	0.4	H_2O	H_2O_2/Fe^{2+}	5	52
M33	Methanethiol	2.0	0.4	H_2O	Air	4	17

[a] PTAA was prepared by irradiation from a ^{60}Co source and contained 1 double bond per 2.5 N atoms as estimated by reaction with excess bisulfite; all reactions were on the HCl form of PTAA.

[b] From IR or microanalysis.

[c] Benzoyl peroxide/dimethylaniline.

TABLE 8. Reaction of 2-Mercaptoethanol (ME) and Thioglycolic Acid (TGA) with PTAA in Water[a]

Expt.	Sulfur compound	Ratio of equivalents of sulfur compound to equivalents N in PTAA	Concn of sulfur compound (M)	Initiator	Reaction time (days)	Reaction (%)
M19	TGA	1	0.8	H_2O_2/Fe^{2+}	0.67	100
M25	TGA	2	1.4	Air	3	100
M27	ME	3.3	2.0	Air	3	100
M28	ME	3.3	2.0	H_2O_2/Fe^{2+}	3	90
M29[b]	ME	3.3	2.0	Air	3	8

[a] PTAA prepared by redox polymerization and contained 1 double bond per 1.7 N atoms; percentage reaction calculated from S analysis.

[b] PTAA as free base; PTAA as HCl in all other experiments.

TABLE 9. Reaction of 2-(N,N-Diethylamino)ethanethiol with PTAA[a]

Expt.	Solvent	pH of solution	Initiator	Reaction time (days)	Reaction (%)[b]
M32	Water	3.6	Air	4	32
M49	Water	5.0	Air	0.75	10
M48	Water	6.0	Air	0.75	5
M51	Water	8.2	Air	0.75	5
M55	DMSO	-	Air	0.75	10
M52	Water	6.0	Amido[c]	0.75	5
M79	DMSO/water	-	H_2O_2/Fe^{2+}	0.75	10
M80	DMSO/water	-	Benzoyl peroxide/ dimethylaniline	0.75	5

[a] PTAA prepared by redox polymerization contained 1 double bond per 1.7 N atoms; ratio of equivalents of thiol to equivalents of N in PTAA was 2.9; concentration of thiol was 1.6 M.

[b] For M32, the percentage reaction was calculated from sulfur analysis; for all others the percentage reaction was estimated from IR spectral analysis.

[c] Amido = azobisisobutyramidinium dihydrochloride; heated at 70°C.

The results of the reaction of some thiols with PTAA are shown in Table 7. The products were intially examined by infrared spectroscopy, from which an estimate of the extent of reaction to within ± 10% was made. Where substantial reaction had occurred, the resin was analyzed for sulfur and, in some cases, then reacted with excess bisulfite and re-analyzed for sulfur. The extent of the double bond reacted was then calculated from these results. Although thiophenol and especially thioacetic acid usually react readily with olefins [8] no reaction was found with PTAA. With a crosslinked resin such as PTAA steric factors will have an important effect on reactivity of a thiol and this in turn depends on the solvent in which the reaction is carried out since this affects the swelling of the resin. The better reaction of methanethiol in water (M33) compared to thiophenol (in methanol) with PTAA may be explained by the fact that water is a better swelling agent than methanol for PTAA (as the HCl). The fact that greater reaction of methanethiol occurred in the presence of a redox initiator (M21) than in its absence (M33) indicates that it is a free-radical reaction. Only 18% reaction of hydrogen sulfide with PTAA occurred in the presence of a redox initiator (M24) but no reaction was detected on UV irradiation which is probably a consequence of the poor UV penetration into the crosslinked resin.

Table 8 shows that 2-mercaptoethanol (ME) and thioglycolic acid (TGA) reacted rapidly and quantitatively with PTAA. Both of these reagents are readily soluble in water and therefore the use of water, which is the best swelling agent for PTAA·HCl, facilitated the reaction. Table 8 shows that air is a sufficient initiator for the reaction with both TGA (M19 and M25) and ME (M27 and M28). The failure of ME to react with the free base form of PTAA (M29) is probably a consequence of the fact that the resin in this form is not swollen in water. The resin obtained from reacting ME with PTAA (M27) was inert to reaction with sulfite.

Since 2-(N,N-diethylamino)ethanethiol hydrochloride is readily soluble in water, quantitative reaction similar to that observed for thioglycolic acid and 2-mercaptoethanol was expected. However, no better than 32% reaction was achieved under a variety of conditions (Table 9). The fact that the extent of reaction does not increase as the pH of the solution was increased indicates that the electrostatic repulsion of the charged resin and thiol is not the major factor contributing to the low extent of reaction. Probably the major factor is a steric one. The extent of reaction was not increased by the use of different solvents such as methanol, DMF and DMSO or the addition of redox or azo type initiators.

CONCLUSIONS

Bisulfite and thiols add by a free-radical mechanism to the pendant allyl groups of PTAA. Bisulfite, 2-mercaptoethanol, and thioglycolic acid add quantitatively, whereas thiophenol is inert. The order of reactivity is HSO_3^-, $HSCH_2CH_2OH$ and $HSCH_2CO_2H$, $\gg$ CH_3SH, H_2S and $HSCH_2CH_2N(C_2H_5)_2$ $>$ CH_3COSH, and C_6H_5SH.

ACKNOWLEDGMENTS

The skilled technical assistance of Mrs. S. Duck and Mr. P. S. K. Ho is acknowledged.

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