JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 2609-2621 (1971)

Aminimides. XI. Modified Polystyrenes Containing Pendent Aminimide or Isocyanate Residues*

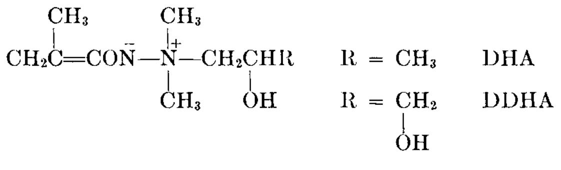
B. M. CULBERTSON and N. A. RANDEN,
Research Center, Ashland Chemical Company,
Minneapolis, Minnesota 55420

Synopsis

The hydrochloride salt of 1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide (DHA) was synthesized and shown to readily homo- and copolymerize with styrene to produce soluble polymers containing pendent quaternary ammonium groups. These polymers may be treated with base to provide modified polystyrenes containing pendent aminimide residues. The latter polymers may be thermolyzed in solution or in the solid phase to produce modified polystyrenes containing pendent isocyanate groups. If the thermolysis is carried out in the presence of "isocyanate reactive" moieties, high molecular weight, crosslinked polymers may be synthesized. The reactivity ratios of DHA · HCl with styrene were determined: $r_1 = 0.33$ and $r_2 = 0.35$. The Alfrey-Price Q and e values were also calculated: $Q = 0.88$ and $e = 0.67$.

INTRODUCTION

Recently, a new synthetic procedure was developed for preparing aminimides.[1] This procedure employed the treatment of esters with equimolar amounts of N,N-dimethylhydrazine and an epoxide. Using this method, the monomers dimethyl-2-hydroxypropylammonium-N-methacryloylimine [1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide, DHA] and dimethyl-2,3-dihydroxypropylammonium-N-methacryloylimine [1,1-dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide, DDHA]



$$\mathrm{CH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CO}\overset{-}{\mathrm{N}}{-}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\overset{+}{\mathrm{N}}}}{-}\mathrm{CH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{R} \qquad \mathrm{R} = \mathrm{CH_3} \quad \mathrm{DHA} \qquad \mathrm{R} = \underset{\mathrm{OH}}{\mathrm{CH_2}} \quad \mathrm{DDHA}$$

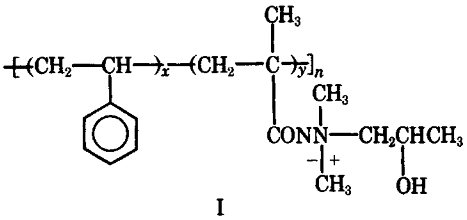
were prepared and their homo- and copolymerization properties studied.[2] These studies showed that DHA, with Q and e values of 0.12 and −2.45, will readily copolymerize with a number of monomers to give a variety of new and useful reactive copolymers with pendent aminimide residues.

---

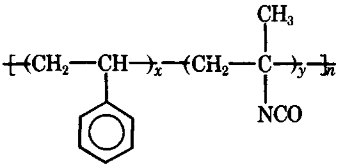
* Presented in part at the Division of Organic Coatings and Plastics Chemistry of the 161st National Meeting of the American Chemical Society, Los Angeles, California, March 1971.

Further, these copolymers may be thermolyzed, both in solution and the solid phase, to give polymers with pendent isocyanate groups.[2]

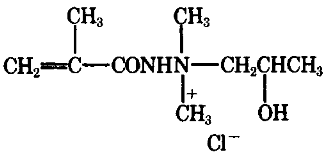
Both laboratory work and simple calculations, using the Alfrey-Price equations[3] and *Q* and *e* values of DHA and styrene, show that DHA will not copolymerize with styrene. Thus, the present work was undertaken to find ways to use DHA in preparing poly(styrene–co-DHA) (I) and poly(styrene–co-isopropenyl isocyanate) (II) copolymers. To do this, the homo- and copolymerization properties of 1,1-dimethyl-1-(2-hydroxypropyl)methacrylylhydrazinium chloride (DHA·HCl) have been studied:



I



II



$CH_2{=}C(CH_3){-}CONH\overset{+}{N}(CH_3)_2{-}CH_2CH(OH)CH_3\ Cl^-$

DHA·HCl

Since molecules with residues of the type $—CONHNR_3^+X^-$ may be treated with base to obtain compounds with the aminimide moiety $(-CO\overset{-}{N}\overset{+}{N}R_3)$,[4–6] it is readily apparent that a monomer such as DHA·HCl should also have utility to prepare reactive polymers with pendent quaternary, aminimide, or isocyanate groups.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colorado. Differential thermal and thermogravimetric analyses were obtained on the du Pont 900 DTA and 950 TGA units, under nitrogen at heating rates of 15°C/min and 5°C/min, respectively. Gel permeation chromatography (GPC) results were obtained on a Waters' Model 200 unit using tetrahydrofuran solvent at room temperature and 4-ft columns of 10^6, 5×10^4, 10^3, 250, and 60 Å porosity Styragel resins. Inherent viscosities (η_{inh}), unless otherwise noted, were determined at 30°C using 0.5 g polymer per 100 ml solvent. The thin-layer chromatography (TLC) method employed silica gel-coated plates, methanol solvent, and I_2 developer. Isocyanate determinations were accomplished as reported earlier.[7]

1,1-Dimethyl-1-(2-hydroxypropyl)methacrylhydrazinium Chloride (DHA·HCl). A solution of DHA and methanol was purged for ca. 0.25 hr with nitrogen before an excess of hydrogen chloride gas was slowly bubbled through the solution over a 3 to 4 hr period. The reaction mixture was concentrated at reduced pressure and the viscous water white material was dried in the presence of NaOH in vacuo to yield a brittle glassy material, DHA·HCl. The infrared spectrum exhibited characteristic absorption bands at 3350, 3210, 1690, 1630, and 1540 cm^{-1}, and the NMR spectrum (D_2O and $CDCl_3$) showed vinyl proton peaks centered at 5.78 and 5.87 ppm, respectively.

ANAL. Calcd for $C_9H_{19}N_2O_2Cl$: C, 48.55%; H, 8.60%; N, 12.58%; Cl, 15.93%. Found: C, 48.35%; H, 8.60%; N, 12.34%; Cl, 16.06%.

A methanol solution containing 2.4 g DHA·HCl was treated with methanolic sodium hydroxide until the solution was basic to litmus paper. The solvent was removed at reduced pressure and the residue extracted with benzene. The latter upon concentration at reduced pressure gave 1.24 g (69.3% yield) DHA which was recrystallized from benzene. Its infrared spectrum was identical with that of an authentic sample of DHA.

Comonomers. The comonomers were used as received from the suppliers for the typical copolymerizations. Styrene was distilled and used immediately for the determination of the Alfrey-Price *Q* and *e* values.

Solvents and Initiators. All of the solvents and azobisisobutyronitrile (AIBN) were used as received from the supplier except for the determination of the Alfrey-Price *Q* and *e* values, in which case they were redistilled at reduced pressure and recrystallized, respectively.

Homopolymerization of DHA·HCl. A reaction flask charged with 30.0 g (0.16 mole) DHA and 36 g ethyl cellosolve was purged with nitrogen for 0.25 hr and concentrated hydrochloric acid (16.6 ml, 0.2 mole) was added, causing the pot temperature to rise 26°C. Fifteen minutes later, the slow nitrogen stream was resumed and the reaction mixture was heated to 80°C. The initiator, 0.24 g AIBN, was added, and after 1 hr, the pot temperature was increased to 100°C. One hour later, 0.03 g AIBN was added to the reaction mixture. After a total reaction time of 4 hr, the solution was allowed to cool to room temperature. Thirty grams of this solution was poured into 200 ml of vigorously stirred acetone. The precipitate was filtered, washed with 300 ml of acetone, and dried in vacuo. The polymer was taken up in methanol and precipitated into 400 ml of vigorously stirred acetone. The precipitated polymer was filtered, washed with acetone, and dried in vacuo to yield 13.4 g (90.0% yield based on portion isolated) poly(DHA·HCl). The infrared spectrum (film) exhibited characteristic absorption bands at 3200, 1690, 1655, and 1540 cm^{-1}.

ANAL. Calcd for $(C_9H_{19}N_2O_2Cl)$: N, 12.58%. Found: N, 12.50%.

The remaining polymer solution, poly(DHA·HCl), was treated with 40 ml of 10% methanolic sodium hydroxide and stirred for 6 hr. After filtering to remove salt and concentrating the filtrate in vacuo, the viscous solution was poured into ether. The precipitate was collected, washed with 50% ether–acetone, and dried in vacuo. The infrared spectrum (film) exhibited the typical strong aminimide absorption band at 1570 cm^{-1}. The polymer exhibited an inherent viscosity of 0.27 in methanol (1.00 g polymer per 100 ml solvent).

Homopolymerization of DHA. A flask was charged with 20.0 g (0.107 mole) DHA and 26 g ethyl cellosolve, and the polymerization was initiated with 0.16 g AIBN in the manner described above. The polymer solution was poured into 300 ml ether and the precipitated polymer was collected, washed with 50% acetone–ether, and dried in vacuo to give a 13.1 g yield of poly-DHA. The infrared spectrum (film) of the polymer exhibited a strong aminimide absorption band at 1575 cm^{-1}. The polymer had an inherent viscosity of 0.10 in methanol (1.00 g polymer per 100 ml solvent).

Homopolymerization of DDHA·HCl. A flask was charged with 50.0 g (0.25 mole) DDHA and 60 g 2-propanol. The solution was degassed with nitrogen for approximately 0.25 hr, and 30 ml (0.36 mole) concentrated hydrochloric acid was added. The polymerization, run as noted above, was initiated with 0.4 g (0.0025 mole) AIBN and 0.04 g of the same 2 hr later. The polymer was precipitated into acetone, collected, washed with acetone, and dried in vacuo. The infrared spectrum (film) exhibited characteristic absorption bands at 3200, 1690, and 1550 cm^{-1}.

ANAL. Calcd for $(C_9H_{19}N_2O_3Cl)_n$: C, 45.30%; H, 8.02%; N, 11.72%. Found: C, 45.73%; H, 7.77%; N, 10.88%.

A sample of poly(DDHA·HCl) was taken up in an excess of methanol and treated with methanolic sodium hydroxide until the solution was strongly basic. The solution was titrated with methanolic hydrochloric acid to a pH of ca. 7.5. The solution was filtered, concentrated at reduced pressure, and the polymer solution was poured into acetone. The polymer was collected, washed twice with acetone, and dried in vacuo. Its infrared spectrum (film) had a strong aminimide absorption band at 1570 cm^{-1}. The polymer exhibited an inherent viscosity of 0.21 in water.

Copolymers of DHA·HCl and Styrene (Table I). Flasks were charged with varying mole percentages of styrene, concentrated hydrochloric acid, DHA, and ethyl cellosolve. The polymerizations were initiated with 1 mole-% AIBN in the manner described for DHA. Small portions, usually 50 g, of the polymer solutions were poured into stirred ether. The white quaternary copolymers (DHA.HCl–styrene) were collected, washed with additional ether and with a 50% ether–acetone solution, and finally dried in vacuo. The infrared spectra (films) of each of the copolymers exhibited characteristic absorption bands at 3180, 1740, 1690, 1600, 1550, and 1500 cm^{-1}.

Copolymers Containing DHA and Styrene (Table I). The remaining polymer solutions (above) containing poly(styrene–co-DHA·HCl) were treated with alcoholic potassium hydroxide at room temperature. The methanol was removed at reduced pressure and the solubilized polymers were poured into vigorously stirred water. The precipitated polymers were collected, washed with water until the wash solution was neutral to pH paper, and air dried. The 60 mole-% DHA–styrene copolymer solution was poured into ether and the polymer was collected, washed with 50% ether–acetone solution, and air dried. The infrared spectra (films) of each of the copolymers exhibited characteristic absorption bands at 1600, 1570, and 1500 cm^{-1}. In certain polymers a small amide band was present at 1700 cm^{-1}. The TGA curves of the various polymers showed 70–91% of the theoretical weight loss of N,N-dimethyl-N-(2-hydroxypropyl)amine, dependent upon the copolymer, from 125° to 200°C.

Copolymers Containing Isopropenyl Isocyanate and Styrene (Table I). A reaction flask fitted with an acidic resin bed (Dowex 50W-X8) and an alumina drying bed was charged with 4 parts xylene and 1 part DHA–styrene copolymer. The xylene solution was heated at reflux under a rapid nitrogen stream. The distillate containing xylene and N,N-dimethyl-N-(2-hydroxypropyl)amine was passed through the acidic resin and alumina beds and the purified xylene was cycled back to the reaction flask. After ca. 6 hr, the solution was allowed to cool and the per cent solids and per cent isocyanate were determined (see Table I). The infrared spectra (films) of the copolymers exhibited a strong isocyanate absorption band at 2250 cm^{-1} and a weak urethane absorption band at 1710 cm^{-1}.

The isopropenyl isocyanate–styrene copolymer derived from 10 mole-% DHA–styrene was isolated by pouring 71 g of the thermolyzed polymer solution into 1–1.5 liters of vigorously stirred Skelly-Solve B. The solvent was decanted and the white polymer was washed twice with 500 ml additional solvent in the same manner. The polymer was filtered and dried at reduced pressures to yield 13 g polymer containing 2.61% NCO.

Blends with 15 Mole-% DHA–Styrene (Table II). The copolymer was mixed with varying equivalents of Epon 812 (di- and triepoxide mixture via epichlorohydrin and glycerin), bis(2-hydroxyethyl) azelate (BHA), bis(2-hydroxyethyl) dimerate (BHD), and polyethylenimine, and the mixtures were heated on steel and glass at 160°C for 0.5 hr. The film derived from polyethylenimine did crosslink; however, it yellowed, cracked, and was very brittle and was not considered any further. The infrared spectra (films) of the other heated blends exhibited strong absorption bands at 2250 and 1720 cm^{-1}.

Determination of *Q* and *e* Values for DHA · HCl (Table III). The purified reagents were placed in 100-ml serum bottles with approximately 30 ml ethyl cellosolve and 0.3 mole-% AIBN as follows. The bottles were charged with DHA and solvent and purged with nitrogen for 0.25 hr. Concentrated hydrochloric acid was added and the serum bottles were capped. After 1 hr with occasional shaking, the caps were removed and styrene and AIBN initiator were added. The serum bottles were recapped and placed in a 60 ± 1°C shaker water bath for 0.5 hr. Runs 1 to 3 were left in the water bath for 1.5 hr. All polymerizations were run to give 10% or less conversions.

The copolymers in runs 4 to 10 were isolated by pouring the solutions into a large excess of acetone. The polymers were collected and washed several

TABLE I. Modified Polystyrenes

DHA·HCl, DHA, or isopropenyl isocyanate in polymer, theoretical mole-%	Monomer feed, moles			N in polymer, %	NCO in polymer, %	DHA·HCl or DHA *in* polymer, mole-%	GPC		Solubility[a]			η_{inh}[b]
	DHA	HCl	Styrene				$M_n \times 10^3$	$M_w \times 10^3$	H_2O	MeOH	Acetone	
DHA.HCl–co-styrene												
5	0.10	0.13	1.90	1.81		7.4	1.4	5.0	−	−	∓	
10	0.20	0.28	1.80	3.35		14.0	1.6	4.3	−	±	∓	
15	0.30	0.42	1.70	4.21		18.9			−	+	∓	
20	0.40	0.57	1.60	5.39		26.0			−	+	−	
30	0.60	0.84	1.40	6.69		34.6			−	+	−	
40	0.80	1.00	1.20	7.59		41.2			+	+	−	
50	1.00	1.20	1.00	8.27		47.0			+	+	−	
60	1.20	1.40	0.80	9.14		55.5			+	+	−	

DHA–co-styrene									
5	1.76		6.5	1.6	24.9	−	−	+	0.146
10	2.98		12.0	5.5	21.6	−	−	+	0.151
15	3.32		13.5	3.2	18.9	−	−	±	0.164
20	4.87		20.9	6.4	21.8	−	±	+	0.179
30	6.27		28.5			∓	+	∓	0.225
40	7.60		36.0			∓	+	−	0.187
50	9.18					∓	+	−	0.177
60	9.83		54.5			∓	+	−	0.232
Isopropenyl isocyanate–co-styrene[c]									
5		1.85		9.1	38.9				
10		2.27		15.6	69.4				
10[d]	1.95	2.61		19.0	68.6				
15		3.44		18.6	102.0				
20		4.84		gelled	gelled				

---

[a] +, Very soluble; ±, moderately soluble; ∓, slightly soluble; −, insoluble.

[b] 0.50 g in 100 ml $CHCl_3$ at 30°C.

[c] Polymers in xylene solution.

[d] Isolated polymer.

TABLE II
Polymer Blends[a]

Co-Reactant	Sward[11,12]	Tukon[11,12]	Xylol resistance	Adhesion	Mar resistance	Impact		Conical	
						Face	Reverse	Flex	"T" Bend
Epon 812	62	18.9	1	excellent	good	160	140	pass	pass
BHA	64	15.7	4	good	fair	160	130	pass	pass
BHD	26	4.59	5	good	good	160	120	pass	pass

[a] 15 Mole-% DHA–styrene with 1 equivalent of co-reactant.

TABLE III
Reactivity Study of DHA·HCl

Run no.	DHA, moles	HCl, moles	Styrene, moles	DHA·HCl monomer feed, mole-%	N in polymer, %	DHA·HCl in polymer, mole-%	Polymer mole ratio F ($=M_1/M_2$)	Conversion, %
1	0.01515	0.0307	0.288	5.0	3.69	16.0	0.190	0.12
2	0.0286	0.0572	0.2574	10.0	4.29	19.3	0.239	2.61
3	0.04325	0.0865	0.245	15.0	5.10	24.2	0.319	7.45
4	0.0577	0.115	0.231	20.0	6.29	31.8	0.467	0.72
5	0.0866	0.173	0.202	30.0	7.23	38.65	0.630	2.79
6	0.0768	0.153	0.115	40.0	8.14	45.8	0.845	1.78
7	0.092	0.192	0.092	50.0	9.76	61.8	1.618	2.37
8	0.1150	0.230	0.0766	60.0	8.98	53.8	1.165	1.66
9	0.1344	0.269	0.0576	70.0	9.56	59.55	1.471	4.29
10	0.1152	0.230	0.0288	80.0	10.35	68.4	2.163	6.75

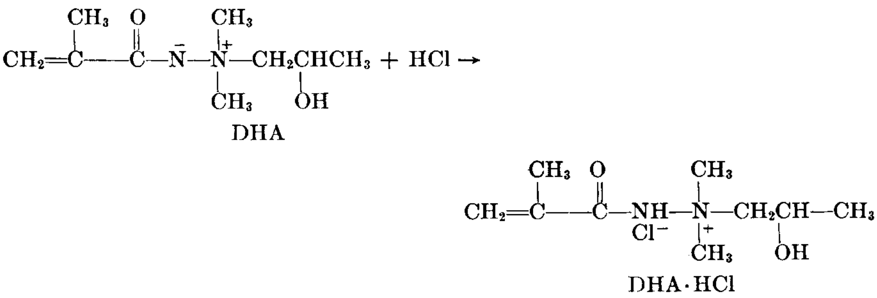
times with acetone. The copolymer in run no. 3 was poured into acetone, collected, and washed several times with ether and finally with acetone. Run no. 2 solution was poured into 15% ether–acetone and the polymer that separated from solution was washed several times with the same solvent mixture. The polymer in run no. 1 was diluted with a 20% ether–acetone mixture and finally precipitated by the addition of ether. The polymer was collected and washed several times with ether. All samples were dried in vacuo and found to be free of monomers by TLC. The infrared spectra (films) of the ten purified polymers exhibited strong characteristic absorption bands at 3180, 1760, 1700, and 1550 cm^{-1}.

Terpolymers Containing DHA, Styrene, and Butyl Acrylate. A reaction flask has charged with 57.3 g (0.55 mole) styrene, 38.5 g (0.30 mole) *n*-butyl acrylate, 28.97 g (0.15 mole) DHA, and 83 ml 2-propanol. This mixture was degassed with nitrogen for 0.25 hr, and 16.7 ml (0.20 mole) of concentrated hydrochloric acid was added. Over a period of 0.25 hr, the pot temperature was raised to 80°C and 1.5 g (~1 mole-%) AIBN was added. The polymerization pot was heated to reflux. Two hours later, 0.15 g additional initiator was added and reflux was continued for 3 hr. The solution was allowed to cool to room temperature and 8 g (0.2 mole) aqueous sodium hydroxide was added. After sitting 16 hr, the polymer solution was poured into water in a Waring blender. The polymer was collected, washed with water until the filtrate was neutral to pH paper, and air dried to obtain a quantitative yield of white solid material. The infrared spectrum (film) exhibited characteristic absorption bands at 1725, 1600, 1568, and 1500 cm^{-1}.

Similar experiments were run with butyl methacrylate giving similar results.

RESULTS AND DISCUSSION

The hydrochloride salt of 1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide (DHA) was generally prepared in situ by treating DHA in ethyl cellosolve with concentrated hydrochloric acid. By using a lower-boiling solvent and gaseous hydrogen chloride, 1,1-dimethyl-1-(2-hydroxypropyl)methacrylylhydrazinium chloride (DHA·HCl),



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\bar{N}-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|+}{N}}}-CH_2\underset{\underset{OH}{|}}{C}HCH_3 + HCl \rightarrow$$

DHA

$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-NH-\underset{\underset{CH_3}{|+}}{\overset{CH_3}{\overset{|}{N}}}-CH_2\underset{\underset{OH}{|}}{C}H-CH_3 \quad Cl^-$$

DHA·HCl

was isolated as a very viscous, water-white material which defied isolation as a crystalline solid. It was finally obtained as a brittle, glassy solid when subjected to stringent drying procedures; however, it reverted back to its previous state upon brief exposures to the atmosphere. The structure of DHA·HCl was verified by its elemental analysis and its infrared and NMR spectra. Its infrared spectrum exhibited the amide absorption bands at 3210, 1690, and 1540 cm^{-1} and the carbon–carbon double bond absorption band at 1630 cm^{-1} and lacked the characteristic band at 1588 cm^{-1} for aminimide. The NMR spectra of DHA·HCl showed that it was not polymeric as evidenced by the vinylic protons centered at 5.78 ppm and 5.87 ppm in D_2O and $CDCl_3$ solvents, respectively.

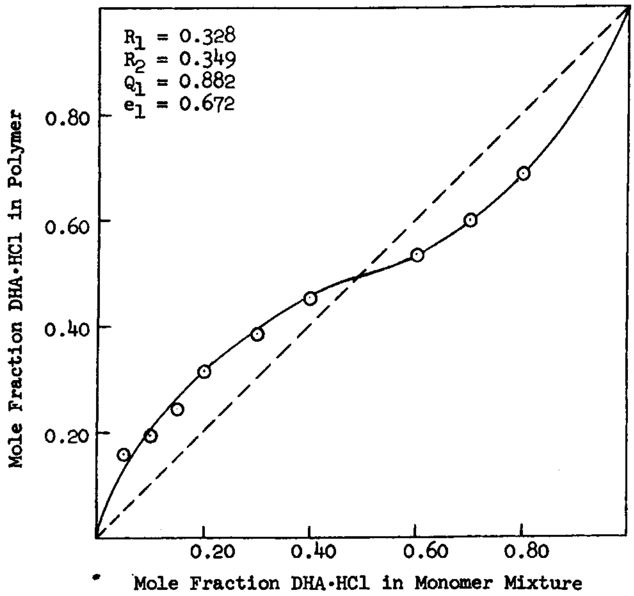


Fig. 1. Copolymer composition curve for the copolymerization of DHA·HCl (M_1) with styrene (M_2) (see Table III).

The reactivity ratios of DHA·HCl monomer (M_1) were determined in the same manner as previously reported[8] using styrene (M_2) as the comonomer. The composition of the monomer feeds and the copolymers obtained for the styrene system are summarized in Table III. In Figure 1, the molar content in the copolymers is plotted against the mole fraction of DHA·HCl in the monomer feed. From these results, the monomer reactivity ratios were obtained by the method of Fineman and Ross: $r_1 = 0.33$ and $r_2 = 0.35$. The Alfrey-Price Q and e values for DHA·HCl obtained from the monomer reactivity ratios were $Q = 0.88$ and $e = 0.67$. The Q and e values of styrene[10] used in the calculations were $Q = 1.000$ and $e = -0.800$.

One can see from the Q and e values that the polymerization characteristics of DHA·HCl differ greatly from those of DHA ($Q = 0.12$, $e = -2.45$).

The latter has a large negative *e* value previously attributed[2] to the electron-repelling tendency of the aminimide $(\text{—}\overset{-}{\text{N}}\text{—}\overset{+}{\text{N}}\langle)$ group, while predictably DHA·HCl is a more reactive monomer ($Q = 0.88$) having a large positive *e* value and resembles methacrylamide ($Q = 1.46$, $e = 1.24$)[10] in its reactivity. It can further be shown from monomer reactivity ratios[9] that DHA will not readily copolymerize with styrene and a variety of methacrylate esters and that DHA·HCl will readily copolymerize with these same monomers.

The homopolymerization of DHA.HCl was carried out in ethyl cellosolve using AIBN initiator. The infrared spectrum of the isolated polymer exhibited the expected amide absorption bands at 3200, 1690, 1655, and 1540 cm^{-1}. The nitrogen analysis also agreed with the expected value. A sample of this polymer was dissolved in methanol and treated with methanolic potassium hydroxide to obtain the respective poly(dimethylhydroxypropylamine methacrylimide).[2] The infrared spectrum of the latter, with a strong absorption band at 1570 cm^{-1} and no amide absorption bands, agreed with the spectrum of poly(DHA) obtained from the polymerization of DHA and supported the polymer structure of DHA·HCl:

$$\text{DHA} \xrightarrow{\text{AIBN}} \text{poly(DHA)} \xleftarrow{\text{base}} \text{poly(DHA·HCl)} \xleftarrow{\text{AIBN}} \text{DHA·HCl}$$

The monomer, DHA·HCl as shown previously, copolymerized with styrene in high conversion to form a low molecular weight copolymer. The general applicability of this sequence to prepare poly[(dimethylhydroxypropylaminemethacrylylhydrazinium chloride)–co-styrene] copolymers were demonstrated by a series of such copolymers listed in Table I. The infrared spectra (films) of each of these copolymers exhibited amide as well as aromatic absorption bands.

A second series of modified polystyrene copolymers, containing pendent aminimide residues, was prepared from the first series simply by treating the latter with base in the appropriate solvent. In this manner, poly(dimethylhydroxypropylamine methacrylimide–co-styrene) copolymers were obtained which could not be prepared directly via the polymerization of DHA and styrene. These copolymers are also listed in Table I along with their physical data. The infrared spectra of each of the copolymers contained the strong aminimide absorption band at 1570 cm^{-1}. Also present in some of the polymers was a weak band at 1700 cm^{-1} attributable to small amounts of the amide functionality which was not completely converted to aminimide. Thermogravimetric analysis and DTA showed that the polymers started losing N,N-dimethyl-N-(2-hydroxypropyl)amine at ca. 125°C and that the different polymers lost between 71% and 95% of the theoretical amount of amine over the range of 125–200°C. The theoretical loss of amine was not achieved because the liberated amine was momentarily held in the polymer melt and reacted with NCO present. This was exemplified by the infrared spectra of the copolymers when thermolyzed on salt plates at 160°C for 0.5 hr. The spectra lacked the aminimide absorption band at 1570 cm^{-1} but did contain the strong isocyanate band at 2250 cm^{-1} and a weak band at 1700 cm^{-1}, attributable to urethane residues.

The third type of modified polystyrene, containing pendent isocyanate groups, was prepared by thermolyzing poly[(1,1-dimethyl-1-(2-hydroxypropyl)amine methacrylimide)–co-styrene] copolymers in refluxing xylene. The liberated amine was removed from the xylene distillate by passing the latter through a cationic resin bed and cycling the xylene back to the reaction. The poly[(isopropenyl isocyanate)–co-styrene] copolymers prepared in this manner are listed in Table I, along with their physical data. Those poly(DHA–co-styrene) materials with less than 20 mole-% DHA were easily thermolyzed, and the isocyanate-containing copolymers exhibited excellent shelf stability when stored under nitrogen, in metal containers, while the 20 mole-% copolymer started gelling during thermolysis. The infrared spectra of these polymers exhibited a strong isocyanate absorption band at 2250 cm^{-1}, a weak urethane band at 1700 cm^{-1}, and strong aromatic absorption bands. Again the urethane band indicated that a small percentage of the liberated hydroxypropylamine reacted with isocyanate moieties during the thermolysis. Correspondingly, the isocyanate contents of the polymers were below the theoretically expected values. One poly[(isopropenyl isocyanate)–co-styrene] sample was isolated from Skelly-Solve B. The infrared spectrum of the dried polymer exhibited the expected isocyanate, aromatic, and urethane bands.

The molecular weights of the poly(dimethylhydroxypropylamine methacrylimide–co-styrene) copolymers were not exceedingly high as evidenced by the GPC data. Better films would be formed from these copolymers if the molecular weights were higher or if the polymers could be crosslinked. The latter was achieved by blending, for example, a 15-mole-% DHA–styrene material with bis(2-hydroxyethyl) azelate, bis(2-hydroxyethyl) dimerate, or Epon 812 and curing these on a support (steel and glass) at 160°C for 0.5 hr. The isocyanate generated from the aminimide should subsequently react with the diol or epoxide to form a crosslinked polymer. This did occur as evidenced by the properties of the resulting polymers (see Table II) and the infrared spectra of the same. The spectra still contained strong NCO absorption bands at 2250 cm^{-1} but also contained a stronger band at ca. 1700 cm^{-1}, indicative of a urethane grouping. Of the blends, the one containing 1.0 equivalent of Epon 812 to 1.0 equivalent of 15 mole-% DHA–styrene had the best film characteristics. It had excellent gloss and adhesion and was quite durable as indicated by the Sward,[11] Tukon,[11,12] and impact data.

Terpolymers were also synthesized using DHA·HCl. The latter was polymerized with styrene and butyl acrylate and with styrene and butyl methacrylate. The terpolymers were treated with base and isolated from water. They exhibited the expected infrared absorption bands for aminimide, ester, and aromatic groups. Thermolysis of the terpolymers at 165°C/0.5 hr gave new terpolymers with pendent isocyanate groups.

Treatment of 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide (DDHA) and hydrogen chloride gave 1,1-dimethyl-1-(2,3-dihydroxypropyl)methacrylylhydrazinium chloride (DDHA·HCl). This hydrochloride salt was homopolymerized with AIBN initiator to obtain poly (DDHA·HCl). The infrared spectrum (nujol) of the latter exhibited amide absorption bands at 1690 and 1550 cm^{-1} and lacked the carbon double bond absorption band at 1620 cm^{-1}. Treatment of poly(DDHA·HCl) with base gave poly(DDHA) whose infrared spectrum lacked the amide absorption bands but did contain the band at 1580 cm^{-1}, attributed to aminimide groups.

In conclusion, DHA·HCl has been shown to be a very reactive, acidic monomer which should be useful in preparing a variety of other copolymers containing either the quaternary, aminimide, or isocyanate pendent groups. It was also demonstrated that polymers containing the pendent aminimide groups could be thermolyzed with substrates containing "isocyanate reactive" moieties to form high molecular weight, crosslinked polymers.

The authors are indebted to P. J. Menardi, M. R. Hallwachs, and D. L. Gregerson for excellent technical assistance during this work.

References

1. R. C. Slagel, *J. Org. Chem.*, **33,** 1374 (1968).
2. B. M. Culbertson, E. A. Sedor, and R. C. Slagel, *Macromolecules,* **1,** 254 (1968).
3. T. Alfrey, Jr., and C. C. Price, *J. Polym. Sci.*, **2,** 101 (1947).
4. S. Wawzonek and R. G. Gueldner, *J. Org. Chem.*, **30,** 3031 (1965).
5. M. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 880 (1965).
6. W. J. McKillip, L. M. Clemens, and R. Haugland, *Can. J. Chem.*, **45,** 2613 (1967).
7. B. M. Culbertson and R. E. Freis, *Macromolecules,* **3,** 715 (1970).
8. B. M. Culbertson and R. C. Slagel, *J. Polym. Sci. A-1,* **6,** 363 (1968).
9. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5,** 269 (1950).
10. L. J. Young, *J. Polym. Sci.*, **54,** 444 (1961).
11. H. A. Gardner and G. G. Sward, *Paint Testing Manual,* 12th ed., Gardner Laboratory, Inc., Bethesda, Md., 1962.
12. P. Fink-Jensen, *Pure Appl. Chem.*, **10**(3), 24 (1965).

Received March 22, 1971
Revised April 21, 1971; June 9, 1971