Table VI
Isothermal Aging of Polyaryloxysilanes Based on *p,p'*-Biphenol

Silyl units (%)	Polymer type	Weight retention at 300°, %	Solubility in benzene	Weight retention at 200°, %	Solubility in benzene
Diphenyl (100)	*a*	86	...	93	+
Dimethyl (100)	*a*	74	...	95	+
Dimethyl (50),	*a*	94	...	74	+−
methylvinyl (50)	*b*	91	...	78	−
Diphenyl (50),	*a*	88	...	78	−
methylallyl (50)	*b*	86	...	91	−
Diphenyl (50),	*a*	91	...	91	+−
methylvinyl (50)	*b*	84	...	83	−
Dimethyl (50),	*a*	97	...	88	−
methylallyl (50)	*b*	95	...	80	−

[a] Uncross-linked. [b] Milled with three parts of dicumyl peroxide, then cured for 1–2 hr at 160°.

out noticeably degrading, but only under anhydrous inert atmospheres. When heated at similar temperatures in ambient air, slow hydrolyses can occur, producing soluble, fusible polymers having reduced molecular weights as well as volatile hydrolysis products. Above about 225°, either in the presence or absence of air or moisture, chain scissions, pendent group cleavage, and cross-linking reactions can occur. The degradation products are insoluble and infusible residues plus low-molecular weight volatiles. The cross-linking reactions appear to occur more rapidly at the higher temperatures. This probably accounts for the reduced weight losses sometimes experienced by the polymers at higher temperatures during isothermal aging. In the case of the unsaturated polymers, it seems likely that oxygen plays a role in the cross-linking reactions observed to occur at as low as 200°.

A more critical study of the stabilities of these polymers is in progress, with particular emphasis on determining the effects of structural modifications on their thermal and hydrolytic resistance. In addition, syntheses and evaluations of polyaryloxysilanes cross-linked through condensation reactions are being pursued. The results of these two complementary studies will be presented in a subsequent paper.

Acknowledgment.—The authors wish to thank the National Aeronautics and Space Administration (under Contract No. NAS8-11837) and the Battelle Memorial Institute for their financial support of this work.

Aminimides. VII.[1a] Homo- and Copolymerization Studies on 1,1-Dimethyl-1-(2-hydroxypropyl)amine–Methacrylimide and 1,1-Dimethyl-1-(2,3-dihyroxypropyl)amine–Methacrylimide[1b]

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ABSTRACT: Two new aminimide monomers have been homo- and copolymerized to soluble polymers containing pendant aminimide groups along the backbone of the chain. The polymers have been drawn into films and thermalized to provide films with increased hardness and adhesion over the unmodified base polymer. The reactivity ratios of each monomer (M_1) with methyl methacrylate (M_2) were determined: 1,1-dimethyl-1-(2-hydroxypropyl)amine–methacrylimide, $r_1 = 0.00$, $r_2 = 1.99$; 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine–methacrylimide, $r_1 = 0.04$, $r_2 = 1.60$. The Alfrey-Price Q and e values were also calculated: $Q = 0.12$, $e = -2.45$ and $Q = 0.24$, $e = -1.24$, respectively. This work further indicates the potential of aminimide monomers for the preparation of "reactive polymers."

A number of studies have shown that both aliphatic and aromatic compounds with nitrogen imine residues of type $-CON^{-}N^{+}R_3$ suffer a carbon–nitrogen migration reaction during pyrolysis,[2-4] yielding tertiary amines and isocyanates. Two prior publications in this

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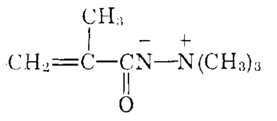
(1) (a) Presented in part to the Organic Coatings and Plastics Chemistry Division at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., March–April 1968. (b) For paper VI in this series, see R. C. Slagel, *J. Org. Chem.*, **33**, 1374 (1968), and Abstracts, 155th National Meeting of the American Chemical Society, Organic Chemistry Division, San Francisco, Calif., March–April 1968, Abstract 186.

(2) S. Wawzonek and R. G. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965).

(3) M. S. Gibson and A. W. Murry, *J. Chem. Soc.*, 880 (1965).

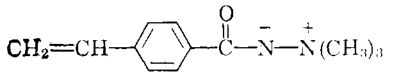
(4) W. J. McKillip, L. M. Clemens, and R. Haugland, *Can. J. Chem.*, **45**, 2613 (1967).

series[5,6] described the preparation and polymerization properties of trimethylammonium-N-methacryloylimine (I, trimethylamine–methacrylimide) and trimethylammonium-N-(4-vinylbenzoyl)imine (II, trimethylamine–4-vinylbenzimide).[7] In the prior work, which demonstrated utility of nitrogen imine monomers for preparing reactive polymers, monomers I and II were prepared by modified versions of the Hinman[8] and Appel[9,10] procedures.



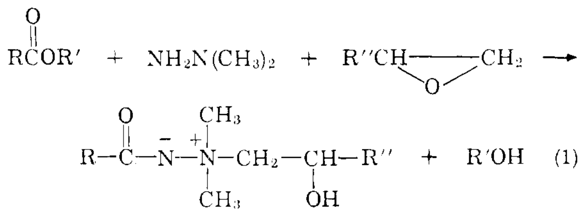
$CH_2{=}C(CH_3)-C(=O)-\overset{-}{N}-\overset{+}{N}(CH_3)_3$

I



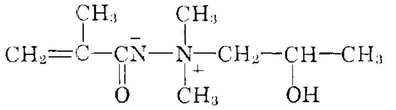
II

Recently, a new and more economical procedure has been discovered in this laboratory for the synthesis of a variety of nitrogen imine monomers[1b] (eq 1). Two



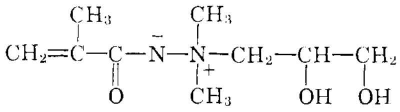
(1)

of the more interesting monomers prepared by this new procedure are dimethyl-2-hydroxypropylammonium-N-methacryloylimine (III, 1,1-dimethyl-1-(2-hydroxypropyl)amine–methacrylimide) and dimethyl-2,3-dihydroxypropylammonium-N-methacryloylimine (IV, 1,1-dimethyl-1-(2,3-dihydroxypropyl)amine–methacrylimide).[7] The preparation, homo- and copolymerization characteristics of these new monomers, including an estimate of their Alfrey–Price *Q* and *e* values, are described in this paper.



$CH_2{=}C(CH_3)-C(=O)-\overset{-}{N}-\overset{+}{N}(CH_3)_2-CH_2-CH(OH)-CH_3$

III



$CH_2{=}C(CH_3)-C(=O)-\overset{-}{N}-\overset{+}{N}(CH_3)_2-CH_2-CH(OH)-CH_2OH$

IV

Experimental Section

The nmr spectra were obtained on a Varian A-60A spectrometer using tetramethylsilane as an internal standard except with deuterium oxide as a solvent where 3-trimethylsilyl-1-propanesulfonic acid was used as the standard. The infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The melting points are uncorrected. Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colo. Differential thermal and thermalgravimetric analyses were obtained on a Du Pont 900 DTA and 950 TGA unit under nitrogen at a heating rate of 20°/min.

I. Monomers. 1,1-Dimethyl-1-(2-hydroxypropyl)amine–Methacrylimide (III). A mixture of 10.0 g (0.1 mol) of methyl methacrylate, 6.0 g (0.1 mol) of 1,1-dimethylhydrazine, and 5.8 g (0.1 mol) of propylene oxide in 50 ml of isopropyl alcohol was placed in a pressure bottle and stirred at room temperature for 72 hr. Evaporation of the solvent *in vacuo* gave 18.2 g (98%) of product. Three recrystallizations from ethyl acetate gave mp 146.5–147.5°. When the reaction was run at 80° for 2 hr, a 95% yield was obtained. The infrared spectrum (halocarbon mull) showed OH stretching at 3130, vinyl proton absorption at between 3100 and 3000, NCH_3 at 2780, C=C at 1645, and aminimide absorption at 1580 cm^{-1}. The nmr spectrum ($CDCl_3$) showed a doublet at τ 8.78 ($CHCH_3$), split peak at 8.12 ($CCCH_3$), peaks at 6.69, 6.63, 6.58, and 6.18 due to NCH_2, N-methyl absorption at 6.43, multiplet at 5.63 (>CH), vinyl proton at 4.92 and 4.28, and the hydroxyl proton at 3.35 ppm. The area ratio was that expected. The DTA curve showed an endotherm at *ca.* 147 and exotherms at 160 and 181. The TGA curve gave an onset of decomposition at 140 with the midpoint at 185°.

Anal. Calcd for $C_9H_{18}N_2O_2$: C, 58.00; H, 9.73; N, 15.10. Found: C, 58.13; H, 9.68; N, 15.14.

1,1-Dimethyl-1-(2,3-dihydroxypropyl)amine–Methacrylimide (IV). Method A. To a stirred solution of 218 g (1.56 mol) of glycidyl methacrylate and 900 ml of isopropyl alcohol was added dropwise to a solution of 125 g (2.09 mol) of 1,1-dimethylhydrazine in 100 ml of isopropyl alcohol. The addition took 2 hr at which time the temperature of the solution had risen 10°. The reaction mixture was stirred at room temperature, resulting in precipitation of a white solid after about 8 hr. After 96 total hr of stirring, the white solid was collected by filtration. The mother liquor, after reduction by one-half, produced a second crop of product. The white crystalline solid (both crops) was collected in a 196 g (62%) yield, mp 116–120°. The aminimide was recrystallized from methanol–ethyl acetate in the ratio of 100 g of solid to 100 ml of methanol and 500 ml of ethyl acetate, yielding 180 g (57% yield) of white crystalline solid, mp 122–123.5°. The infrared spectrum (halocarbon mull) showed bands due to the hydroxyl grouping at 3280, NCH_3 grouping at 2780, vinyl grouping at 1635, and the aminimide carbonyl at 1550 cm^{-1}. The nmr spectrum (DMSO-d_6) exhibited a singlet at 8.18, a multiplet at 6.5, a singlet at 6.25, multiplet at 5.88, multiplets at 4.94 and 4.3 (vinyl), and singlets at 5 and 3.98 ppm (OH) in the expected ratios of 3:1:1:1:2:2. The TGA curve exhibited an onset of decomposition at 155° with the midpoint at 200°.

Anal. Calcd for $C_9H_{18}N_2O_3$: C, 53.45; H, 8.97; N, 13.85. Found: C, 53.58; H, 9.10; N, 13.92.

Method B. A mixture of 25 g (0.25 mol) of methyl methacrylate, 15 g (0.25 mol) of 1,1-dimethylhydrazine, and 18.5 g (0.25 mol) of glycidol in 200 ml of *t*-butyl alcohol was stirred at room temperature for 60 hr. The mixture was cooled in an ice bath and the white solid collected by filtration and washed with anhydrous ether, yielding 33 g. The mother liquor was reduced to a heavy oil on the rotory evaporator and the oil dissolved in 5 ml of methanol and

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(5) B. M. Culbertson and R. C. Slagel, *J. Polym. Sci., Part A-1*, **6**, 363 (1968).

(6) B. M. Culbertson, E. A. Sedor, S. Dietz, and R. E. Fries, *ibid.*, in press.

(7) The referees suggested use of the ammonium–imine nomenclature (*e.g.*, A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 266) for naming monomers I–IV. We show both the recommended and more commonly used aminimide nomenclature (in parentheses) at first mention of the monomers. After first mention of the monomers, we preferred to use the aminimide nomenclature.

(8) R. L. Hinman and M. C. Flores, *J. Org. Chem.*, **24**, 660 (1959).

(9) R. Appel, H. Heinen, and R. Schallhorn, *Chem. Ber.*, **99**, 3118 (1966).

(10) H. W. Schiessl and R. Appel, *J. Org. Chem.*, **31**, 3851 (1966)

TABLE I
REACTIVITY STUDY OF MONOMER III

Run no.	Moles of III	Moles of methyl methacrylate	Mole % of III monomer feed	N, %	Mole % of III in polymer	$F = M_1/M_2$ mole ratio of polymer	Conversion, %
1	0.01	0.19	5.0	0.73	2.67	0.2074	3.3
2	0.02	0.18	10.0	1.43	5.35	0.0565	3.6
3	0.03	0.17	15.0	2.06	7.86	0.0853	10.0
4	0.04	0.16	20.0	2.67	10.39	0.116	3.4
5	0.06	0.14	30.0	3.76	15.18	0.179	8.4
6	0.08	0.12	40.0	4.39	18.13	0.221	3.6
7	0.12	0.08	60.0	6.33	28.08	0.390	6.0
8	0.14	0.06	70.0	7.83	36.85	0.583	5.3
9	0.16	0.04	80.0	8.29	39.76	0.660	9.8

100 ml of ethyl acetate. Cooling yielded 8 g. The crude aminimide (41 g) was obtained in an 81% yield, mp 122–123°. The analyses were the same as for Method A.

Comonomers. The monomers methyl methacrylate and acrylonitrile were purified by distillation under nitrogen through a 12-in. Vigreux column immediately before use. Butyl acrylate was used as received from Rohm and Haas Co.

II. Solvents and Initiators. All of the solvents used in the polymerization were purified according to standard procedures. Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

III. Polymerization. A. Polymerizations of 1,1-Dimethyl-1-(2-hydroxypropyl)amine–Methacrylimide (III). 1. Homopolymerization. Into a 100-ml four-necked flask, equipped with a stirrer, thermometer, reflux condenser, and a nitrogen inlet tube, were placed 4.0 g of monomer III in 30 ml of water. Nitrogen was bubbled through the solution for 30 min. A solution of 4 mg of AIBN in 2 ml of acetone was then added and the flask then purged with nitrogen for an additional 15 min. The mixture was heated at 80° for 5 hr. After cooling to room temperature and filtering, the solution was poured into 100 ml of stirred acetone. The white precipitate was collected and washed with acetone to give 3.3 g (82% yield) of polymer. The analytical sample was dissolved in water, reprecipitated in acetone, and dried *in vacuo*. The infrared spectrum (halocarbon mull) showed typical aminimide absorption at 1580 cm^{-1}. The nmr spectrum (D_2O) showed no vinyl protons. The DTA curve exhibited an exotherm at 172°, and TGA showed an onset of decomposition at 155° (midpoint 175°). Thermogravimetric analyses also demonstrated the polymer lost 98% of theoretical N,N-dimethyl-1-amino-2-hydroxypropane when heated from 150 to 200°. The nitrogen analysis gave 14.46% (calcd, 15.10%). The polymer exhibited an inherent viscosity in water of 0.51 (concentration 0.5 g/100 ml, 25°).

2. Copolymer of III and Methyl Methacrylate. Into a 100-ml four-necked flask (equipped as in example 1) were placed 2.0 g of monomer III and 6.6 g of methyl methacrylate in 60 ml of acetonitrile. The flask was purged with nitrogen for 30 min after which 9 mg of AIBN in 1 ml of acetone was added. The polymerization was allowed to proceed at 75° for 5 hr under nitrogen. The solvent was evaporated *in vacuo* to give 4.5 g of a white solid. The solid was dissolved in acetone, filtered, and poured into distilled water to give a white solid which was dried *in vacuo* over phosphorus pentoxide. The nmr spectrum (acetone-d_6) showed no vinyl protons. The infrared spectrum (halocarbon mull) showed ester carbonyl at 1725 and aminimide absorption at 1580 cm^{-1}. The elemental analysis checks for a ratio of III to methyl methacrylate of 1:10.

Anal. Calcd for $C_{59}H_{96}N_2O_{22}$: C, 59.77; H, 8.16; N, 2.36. Found: C, 60.05; H, 8.00; N, 2.30.

The DTA curve showed an exotherm at 183° and an endotherm at 357°. The TGA curve showed an onset of decomposition at 125° and a midpoint at 175°, with a weight loss of 10.5 *vs.* 8.7% for theoretical of N,N-dimethyl-1-amino-2-hydroxypropane.

The polymer was dissolved in chloroform, spread onto a glass plate, and air dried. The film which exhibited a Sward hardness of No. 44 was then pyrolyzed at 160° for 30 min. The infrared spectrum of the resulting film showed loss of aminimide absorption at 1580 cm^{-1} and the appearance of isocyanate absorption at 2250 cm^{-1}. The film was hard (Sward No. of 56) and brittle.

3. Monomer III–Methyl Methacrylate Copolymerization for the Alfrey–Price *Q* and *e* Values (Table I). The purified reactants according to Table I were placed into a 100-ml serum bottle with 80 ml of dimethylformamide and 1% of their total weight of AIBN. The bottles were flushed with dry nitrogen, sealed, and placed in a water bath maintained at 60 ± 0.1° for either 30 min (samples 1–6) or 45 min (samples 7–9) to give 10% or less conversion.

The copolymers were isolated by pouring the solutions into diethyl ether. All samples were washed with boiling hexane. Samples 1–8 were washed further with boiling water while sample 9 was washed with boiling acetone.

Purification of the copolymers varied according to the content of III. Samples 1–6 were precipitated from acetone with water. Sample 7 was washed with hexane, acetone, and boiling water. Sample 8 was precipitated from methanol with diethyl ether and sample 9 from water with acetone. All samples were free of monomer as shown by tlc using silica gel, eluted with methanol, and developed with I_2. All samples were dried *in vacuo* at 70° over phosphorus pentoxide for 22 hr prior to elemental analysis.

B. Polymerizations of 1,1-Dimethyl-1-(2,3-dihydroxypropyl)amine–Methacrylimide (IV). Unless otherwise specified, the polymerizations were carried out in 100-ml serum bottles, purging the solutions first with nitrogen. The bottles were sealed with a rubber septum and heated in an oil bath for the time indicated.

1. Homopolymerization. The monomer IV (3.0 g) was dissolved in 20 ml of methanol along with 0.3 g of AIBN and heated at 70° for 72 hr. The solution was reduced to 10 ml, then poured into 200 ml of ether. The solid was washed with additional ether and dried, yield 2.0 g. The infrared spectrum (film from $CHCl_3$) showed –OH grouping at 3300 cm^{-1}, and carbonyl at 1560 cm^{-1}.

Anal. Calcd for $C_7H_{12}N_2O_3$: N, 13.85. Found: N, 13.29.

The polymerization was repeated using water as a solvent with the same results. A methanolic solution of the polymer (50% solids) was used to coat glass plates. The films (3 mils thick) were dried 3 hr at 22° and 16 hr at 110°, resulting in a Sward hardness of 20. After heating at 170° for 2 hr the films exhibited a Sward hardness of 42. The infrared spectrum showed loss of aminimide carbonyl with formation

TABLE II
REACTIVITY STUDY OF MONOMER IV

Run no.	Moles of IV	Moles of methyl methacrylate	Mole % of IV monomer feed	N, %	Mole % of IV in polymer	$F = M_1/M_2$ mole ratio of polymer	Conversion, %
1	0.01	0.19	5.0	0.98	3.64	0.0377	5.0
2	0.02	0.18	10.0	1.56	5.92	0.0629	7.5
3	0.03	0.17	15.0	2.16	8.38	0.0914	4.5
4	0.04	0.16	20.0	2.94	11.76	0.133	6.0
5	0.06	0.14	30.0	3.82	15.85	0.188	8.2
6	0.08	0.12	40.0	4.38	18.61	0.228	10.0
7	0.06	0.04	60.0	7.39	36.15	0.566	7.5
8	0.07	0.03	70.0	9.10	48.65	0.947	4.0
9	0.08	0.02	80.0	8.55	44.39	0.798	5.5

of the urethane carbonyl grouping. The polymer exhibited an inherent viscosity in water of 0.18 (concentration 0.5 g/100 ml, 25°).

2. Copolymerization of IV and Methyl Methacrylate. Monomer IV (5.0 g) and methyl methacrylate (10.0 g) were dissolved in a mixture of 5 ml of methanol and 50 ml of acetonitrile along with 0.2 g of AIBN. The reaction was carried out at 75° for 65 hr. The solution was poured into 500 ml of ether with stirring and the white solid collected by filtration and air dried, yield 14.0 g. The polymer was dissolved in chloroform and reprecipitated from ether. After air drying the polymer weighed 13 g. The infrared spectrum showed the hydroxyl grouping at 3350 cm^{-1}, the ester grouping at 1720 cm^{-1}, the aminimide carbonyl at 1560 cm^{-1} but no vinyl grouping. The tlc, using methanol or chloroform solvent and I_2 developing agent, showed no trace of monomer. The DTA curve exhibited an exotherm at 193°, and TGA indicated that the polymer loses amino alcohol starting at 150° (midpoint at 195°). The weight loss is 92% of theoretical. On the basis of nitrogen analysis (3.86%), the monomer ratio is estimated at 5:1 of methyl methacrylate to IV (calcd for 5:1: N, 3.95%).

3. Copolymerization of IV and Acrylonitrile. Monomer IV (2.02 g) and acrylonitrile (5.3 g) were dissolved in 35 ml of acetonitrile along with 0.05 g of AIBN. The reaction was carried out at 80° for 18 hr. The polymer was isolated by pouring the viscous solution into a large volume of ether and collecting the precipitated polymer. The polymer was extracted with ether until tlc indicated an absence of free IV. The polymer was readily soluble in polar solvents. A N,N-dimethylformamide solution was used to cast films on glass plates. The dried films exhibited infrared absorption bands at 3400, 2245, and 1575 cm^{-1}, indicative of copolymerization.

The coated plates were heated in an air circulating oven for 2 hr at 175°. The films darkened and became resistant to dimethylformamide solvent. Further, the heated films exhibited weak infrared absorption bands at 3300, 2265, and 1710 cm^{-1} and no absorption band at 1575 cm^{-1}.

4. The Terpolymer from IV, Methyl Methacrylate, and Butyl Acrylate. Monomer IV (3.0 g), methyl methacrylate (7.0 g), and butyl acrylate (10.0 g) were dissolved in 50 ml of acetonitrile along with 0.2 g of AIBN. The reaction was carried out at 70° for 90 hr. The solution was stripped of solvent, and the sticky residue dissolved in 20 ml of chloroform. The polymer was precipitated from ether followed by two additional ether washings and one treatment with hexane. The hardened polymer was dried *in vacuo* (*ca.* 0.1 mm) to remove solvent and give 12.8 g (64% yield) of a white solid showing no monomer by tlc. The infrared spectrum (film) showed ester (1725 cm^{-1}) aminimide (1565 cm^{-1}) and hydroxyl (3300 cm^{-1}) but no vinyl absorption. On the basis of nitrogen analysis (2.29%), the amount of monomer IV in the polymer was estimated to be at least 10 mol %. The polymer exhibited an inherent viscosity in chloroform of 0.50 (concentration 0.50 g/100 ml, 25°).

A solution of 1.0 g of polymer in 5 ml of chloroform was filmed (3 mils thick) on glass, then dried for 2 hr at 22° and 2 hr at 110°. The Sward hardness was 40. After 2 hr at 180°, the Sward hardness increased to 45, and the infrared spectrum showed an isocyanate band at 2250 cm^{-1}. The film was no longer soluble in chloroform. The film, after treatment with methanol for 4 hr, continued to exhibit isocyanate absorption in the infrared spectrum.

5. Monomer IV–Methyl Methacrylate Copolymerization for the Alfrey–Price *Q* and *e* Values (Table II). The runs were made according to the direction given for monomer III (see part A-3).

All samples were isolated by pouring the reaction mixture into diethyl ether. All samples were washed until tlc showed one spot. Samples 1–6 were washed with hexane and then water; samples 7 and 8 were dissolved in water and purified by dialysis; sample 9 was extracted with acetone until free of monomer. The samples were dried and analyzed as before (A-3).

C. Preparation of Copolymers and Their Corresponding Films for Comparison of the Effect of III, IV, and Trimethylamine–Methacrylimide[2] as Polymer Modifiers. The copolymers (Table III) were made with commercial methyl methacrylate with 10 ppm of *p*-methoxyhydroquinone inhibitor (Rohm and Haas) and the purified aminimide in dimethyl formamide. All runs were made with 5% feed moles of aminimide, and all were charged to give 40% solids. The initiator (AIBN) concentration was 1% by weight of total solids. In all cases the reactions were run under nitrogen for 16 hr at 60°

After cooling, the viscous solutions were diluted to a 25% solid level with methyl ethyl ketone. Films were drawn on glass, aluminum, and cold rolled steel with a 3-mil draw down bar. The air dry films were allowed to dry for 16 hr before testing. The baked films were allowed to air dry for 10 min and then baked at 160° for 30 min. All films were clear and colorless except film 3 after baking, which had a pale yellow tint.

The infrared spectra of films 2, 3, and 4, after air drying, showed aminimide absorption at 1580 cm^{-1}. After baking, the same films showed loss of the band at 1580 cm^{-1} and the appearance of a band at 2270 cm^{-1} attributable to isocyanate absorption.

Results and Discussion

A. Monomer Synthesis and Properties. Monomers III and IV were prepared according to eq 1. The method is more fully discussed in ref 1b. Briefly, it is felt that the epoxide and 1,1-dimethylhydrazine (DMH) react first to give the alkoxide V which then tautomerizes

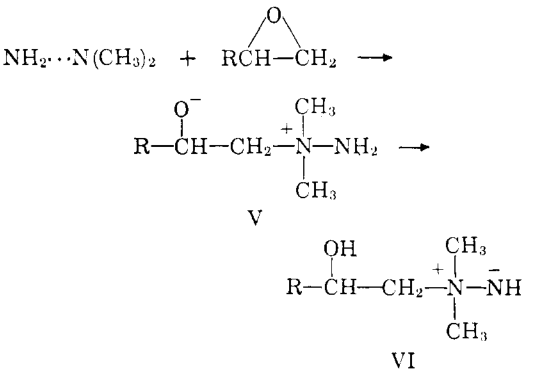
Table III

Comparison of Films of Polymers Modified with Aminimides

Copolymer	η_{inh}[a]	Sward hardness[b] Air dry	Sward hardness[b] 160°/30 min	Adhesion,[c] % Air dry Al	Air dry Steel	Air dry Glass	160°/30 min Al	160°/30 min Steel	160°/30 min Glass
1. Methyl methacrylate (MMA) control	0.45	43	50	1	1	1	7	1	1
2. MMA + III	0.46	48	55	1	1	1	98	80	10
3. MMA + IV	0.36	47	58	7	1	30	99	50	35
4. MMA + I	0.52	44	56	89	60	1	99	98	8

[a] Inherent viscosities determined in chloroform (concentration 0.5 g/100 ml, 25°). The polymers were isolated, purified, dried, and checked for purity according to procedures used in Experimental Sections IIIA3 and IIIB5. [b] Sward hardness values were measured on 3-mil films on glass. [c] Each 3-mil film was cross-hatched with a sharp razor blade. 3M Co. Magic Tape was pressed over the cross-hatched area and pulled up with a slow steady motion. The per cent of the film squares remaining is the figure shown in the table. Accuracy is estimated at ±5%.

to the aminimine VI (eq 2). The nucleophilic aminimine (VI) then attacks the ester to give the resulting aminimide.



$$NH_2\cdots N(CH_3)_2 + RCH\overset{O}{-}CH_2 \longrightarrow R-\underset{}{\overset{O^-}{CH}}-CH_2-\overset{+}{N}(CH_3)_2-NH_2 \ (\mathrm{V}) \longrightarrow R-\overset{OH}{CH}-CH_2-\overset{+}{N}(CH_3)_2-\overset{-}{N}H \ (\mathrm{VI}) \quad (2)$$

Synthesis of III uses methyl methacrylate, DMH, and propylene oxide. Monomer IV may be made from methyl methacrylate, DMH, and glycidol or from glycidyl methacrylate and DMH.

Both monomers III and IV have similar solubility characteristics, although IV is less soluble in the more nonpolar solvents. Both are soluble in water, methanol, ethanol, dimethyl sulfoxide, dimethylformamide, chloroform; slightly soluble in benzene and ethyl acetate; and insoluble in hexane and carbon tetrachloride.

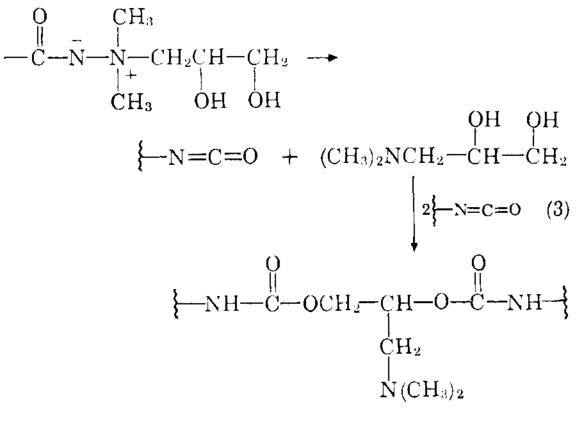
The thermal stability of each monomer is good up to at least 140°. The shelf stability seems to be very good, each monomer having been stored for several months at room temperature without polymer formation.

B. Polymerizations of III. The homopolymerization of III was carried out in water using AIBN as initiator. The infrared and nmr spectra showed the loss of vinyl unsaturation. The infrared spectrum showed that the aminimide function had been retained by the presence of the band at 1580 cm^{-1}. Thermogravimetric analysis (TGA) showed that the polymer started losing N,N-dimethyl-1-amino-2-hydroxypropane at 155°. The weight loss was 98% of theoretical for loss of the amino alcohol.

A copolymer was made with methyl methacrylate in acetonitrile using AIBN as a catalyst. The resulting polymer contained aminimide and ester moieties but no vinyl unsaturation, as determined by infrared and nmr spectroscopy. TGA showed weight loss to start at 125° and to be 83% of theory for loss of the amino alcohol. Elemental analysis showed the polymers to contain a 10:1 ratio of methyl methacrylate to III. The corresponding ratio of the starting monomers was 6:1. These data indicate that III is less reactive than methyl methacrylate. This conclusion was shown to be valid from the reactivity study (Table I, Figure 1).

The solubility and inherent viscosities of the copolymers of III with methyl methacrylate is affected considerably by the amount of III in the polymer. Table IV shows that the polymers are insoluble in highly polar and highly nonpolar solvents at low levels of III. At higher levels of III the solubility increases in polar solvents, as expected for the polar aminimide function, but still is not soluble in nonpolar solvents.

C. Polymerization of IV. The homopolymerization of IV was carried out in methanol or water using AIBN as initiator. Infrared spectroscopy showed the presence of aminimide functionality and the lack of vinyl unsaturation. Pyrolysis of a 3-mil film of the polymer at 170° for 2 hr resulted in the loss of infrared absorption at 1560 cm^{-1} and the appearance or urethane-type absorption band at about 1700 cm^{-1}. This suggests that the film cross-links during pyrolysis, probably as shown in eq 3.



$$-\overset{O}{\overset{\|}{C}}-\overset{-}{N}-\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}-CH_2\underset{OH}{CH}-\underset{OH}{CH_2} \longrightarrow \wr-N{=}C{=}O + (CH_3)_2NCH_2-\overset{OH}{CH}-\overset{OH}{CH_2} \xrightarrow{2\wr-N=C=O} \wr-NH-\overset{O}{\overset{\|}{C}}-OCH_2-\underset{CH_2N(CH_3)_2}{CH}-O-\overset{O}{\overset{\|}{C}}-NH-\wr \quad (3)$$

A copolymer was made with methyl methacrylate in 10:1 acetonitrile–methanol mixture using AIBN as initiator. The resulting polymer contained aminimide and methyl ester functionality but no vinyl unsaturation as determined by infrared spectroscopy. TGA showed weight loss to start at 150° and to be 92% of theory for loss of the amino alcohol. Elemental analysis showed the polymers to contain a 5:1 ratio of methyl methacrylate to IV. The corresponding ratio

TABLE IV

SOLUBILITY OF COPOLYMERS OF III AND IV WITH METHYL METHACRYLATE[a]

Mole % of III and (IV) in polymers	H_2O	CH_3OH	DMF	$(CH_3)_2C{=}O$	$CHCl_3$	Xylene	$(CH_3CH_2)O$	η_{inh}[b]
2.5 (3.5)	−	−	+	+	+	...	...	0.73
5.5 (5.8)	−	−	+	+	+	−	−	0.66
8.0 (8.4)	−	−	+	+	+	−	−	0.53
10.5 (11.9)	−	−	+	+	+	−	−	0.57
15.2 (15.7)	−	+	+	+ (−)	+	−	−	0.50
18.0 (18.4)	−	+	+	+ (−)	+ (−)	−	−	0.48
28.0 (36.0)	−	+	+	−	+ (−)	−	−	0.18
36.8 (48.5)	−	+	+	−	−	−	−	0.23
40.0 (44.2)	+	+	+	−	−	−	−	0.21

[a] + = soluble; − = insoluble; 0.1 g of polymer in 1 g of solvent; solubility of polymers is the same unless in parentheses. [b] The inherent viscosities of III copolymers (2.5–18.0 mol % III) were determined in chloroform and (28.0–40.0 mol % of III) in methanol (concentration 0.5 g/100 ml, 25°). The polymers were isolated, purified, dried, and checked for purity according to procedures used in Experimental Sections IIIA3 and IIIB5.

of the starting monomers was 4:1. As with monomer III, these data indicate that IV is less reactive than methyl methacrylate. Such was shown to be the case from the reactivity study (Table II, Figure 1).

The solubility of the copolymers of IV with methyl methacrylate varies with the amount of IV in the polymer (Table IV). The effect is similar to that of III and methyl methacrylate discussed above.

Two other polymers were made with IV. One was a copolymer with acrylonitrile and the other a terpolymer with methyl methacrylate and butyl acrylate. As before, infrared and nmr spectroscopy indicate the incorporation of the aminimide functionality into the polymer.

D. Determination of Monomer Reactivity Ratios. The reactivity ratios of III and IV were determined in the same fashion as before.[5] The compositions of the monomer feeds and the copolymers obtained for the methyl methacrylate-III or -IN system are summarized in Tables I and II. From these results the monomer reactivity ratios were obtained by the method of Fineman and Ross:[11] $r_1 = 0.00$, $r_2 = 1.99$ for III, and $r_1 = 0.04$, $r_2 = 1.60$ for IV.

In Figure 1 the mole fraction of III and IV in the monomer feeds is plotted against the corresponding mole fraction of III and IV in the copolymer.

The Alfrey-Price Q and e values[12] for III and IV were obtained from the monomer reactivity ratios: $Q = 0.12$, $e = -2.45$ for III and $Q = 0.24$, $e = -1.24$ for IV. The Q and e values of methyl methacrylate[13] used in the calculations were $Q = 0.74$ and $e = 0.40$.

From the Q and e values of trimethylamine-methacrylimide (I, $Q = 0.18$; $e = -0.60$) previously determined by us,[5] one can place the general order of monomer reactivity as IV > I > III. The difference in the e value for these three monomers is difficult to rationalize. However, the negative e values have previously been explained[5] as being due to the electron repelling tendency of the $N^{-}N^{+}<$ grouping. The general reactivity of the methacrylimide monomers in comparison to other methacrylyl-type monomers is shown in Table V.

TABLE V

Q AND e VALUES OF METHACRYLYL MONOMERS

Monomer	Q	e
Methacrylic acid[a]	2.34	0.65
Methacrylamide[a]	1.46	1.24
Sodium methacrylate[a]	1.36	−1.18
Methyl methacrylate[a]	0.74	0.40
N-Methylmethacrylamide[a]	0.32	−0.60
IV	0.24	−1.24
Trimethylamine-Methacrylimide[b]	0.18	−0.60
III	0.12	−2.45

[a] See ref 6. [b] See ref 2.

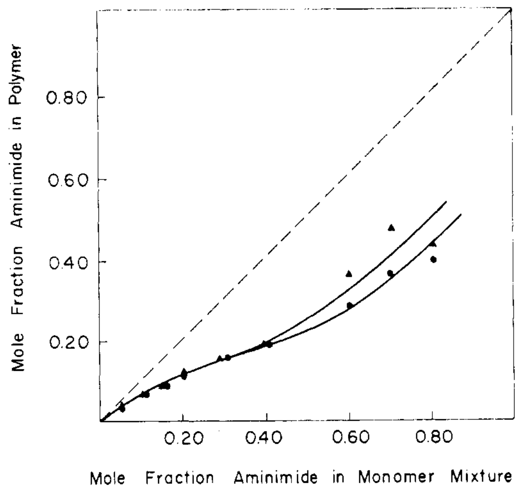


Figure 1. Copolymer composition curve in the copolymerization of III (●) and IV (▲) with methyl methacrylate.

E. Properties of Films Made from Aminimide Copolymers. Films were spread of the various copolymers of III and IV. These include the copolymers of III with methyl methacrylate and of IV with methyl methacrylate and acrylonitrile plus a terpolymer of IV, methyl methacrylate, and butyl acrylate.

Pyrolysis of the copolymers of IV would be expected to give pendant isocyanate groups and a diol which should subsequently react to provide a cross-linked polymer (eq 3). On the other hand, pyrolysis of the copolymers of III should give a monofunctional alcohol not capable of cross-linking the polymer. Because the

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pyrolysis temperature must be over the boiling point of the N,N-dimethyl-1-amino-2-hydroxypropane (bp 126°) one would expect little or no reaction between the alcohol and isocyanate. Instead, the amino alcohol should flash off and leave free isocyanate groupings in the polymer. In the other case (copolymers of IV) the amino diol should not flash off (bp 109–111° at 15 mm) but should remain to react with the pendant isocyanate groups.

The infrared spectra of the various copolymers, pyrolyzed at 160–180°, showed that the reasoning above, with modification, was correct. Strong isocyanate absorption at about 2250 $\mathrm{cm^{-1}}$ was present, as expected, after pyrolysis of the copolymers of III. Contrary to expectation, however, the pyrolyzed copolymers of IV exhibited both a strong isocyanate absorption band at 2250 $\mathrm{cm^{-1}}$ and a weak band at 1710 $\mathrm{cm^{-1}}$, indicative of a urethane grouping. In the case of the copolymers of IV, the presence of the isocyanate absorption can be explained by the low reactivity of the tertiary aliphatic isocyanate group.

Properties of the pyrolyzed and unpyrolyzed films of the copolymers of I, III, and IV with methyl methacrylate were compared along with unmodified methyl methacrylate polymer. The results are shown in Table III. The Sward hardness values of all of the polymers increase upon pyrolysis. The modified methacrylates seem to be slightly harder than the base polymer. This could be due to enhanced van der Waals bonding because of the highly polar aminimide grouping before pyrolysis and isocyanate or urethane grouping after pyrolysis. The most remarkable difference between the base polymer and those modified with aminimides is in adhesion. Here the modified methacrylates show greatly enhanced adhesion after pyrolysis. This may be due to the isocyanate groupings generated by the pyrolysis. These isocyanate groups probably both react chemically with active hydrogen atoms on the substrate surface and interact physically with the surface through van der Waals bonding. The polymer modified with IV was the only one that showed reasonable adhesion to glass, both before and after pyrolysis. This is perhaps due to hydrogen bonding of the larger number of OH groups to the hydrated glass surface. One should also note the enhanced adhesion of the polymer modified with I to aluminum and steel prior to pyrolysis. No explanation is offered.

From the data presented, indications are that the monomers described possess great potential as modifiers of base vinyl polymers, especially in increasing their hardness and their adhesion to varied substrates.

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Colloidal Properties of Styrene–Butadiene Block Copolymers[1]

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ABSTRACT: Styrene–butadiene block copolymers form micelles in selective and in nonselective solvents because of interactions of the different polymer sequences with the solvent or with each other. The formation of micelles has been studied by electron microscopy. The compatibility of random, block, or graft copolymers with the corresponding homopolymers is discussed.

Block and graft copolymers have sequences of different homopolymers in the same molecule. Selective solvents can often be found which are good with respect to one of the homopolymer sequences, but are poor with respect to the other types of sequences. As with soaps and nonionic surfactants, block and graft copolymers are nonuniformly soluble in selective solvents and can show a variety of colloidal properties. They can emulsify oil-water systems,[2] and they can form micelles[3–4] and stabilize organic lattices[5] in which an organic solvent rather than water is the continuous phase. In analogy to conventional surfactants, the colloidal properties of block and graft copolymers in selective solvents have been explained on the basis of their nonuniform solubility,[2–4] *i.e.*, on the basis of polymer–solvent interactions.

Previous work[6,7] has demonstrated that block and graft copolymers can stabilize emulsions of the oil-in-oil type, which consist of phases of immiscible polymer solutions. Such emulsions are obtained by dissolving two chemically different homopolymers and the corresponding block or graft copolymer in a mutual solvent. Since all components are required to be soluble, a nonselective solvent is usually chosen, *i.e.*, a good solvent for both types of polymer chains present in the system. The stability of the resulting "polymeric

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