have not attempted to carry out a similar correction for the compositional contribution of the acid units to ΔT_g, because extensive dimerization of the carboxyl groups also exists in polyacrylic acid and it is impossible to assess independently the compositional effect. Even with these reservations in mind, it is still believed that the increase in T_g can be attributed mainly to the cross-linking effect, as implied by the agreement of our experimental data with the theory of Fox and Loshaek. The smaller proportionality constant between ΔT_g and ρ in our copolymers in comparison with that found for polystyrene or poly(methyl methacrylate) reflects the fact that volume shrinkage accompanying the dimerization of carboxyl groups is less than the volume decrease produced by the introduction of a covalent cross-link. Our results also fit the *empirical* equation of Shibayama and Suzuki[26] which are applicable to many covalently cross-linked polymers

$$T_g = K_1 \ln K_2\rho \qquad (2)$$

We therefore conclude that the dimerization of the acid units in these copolymers raises the T_g of a branched PE chain by a mechanism analogous to the action of covalent cross-links.

Once the T_β has been attained the segmental mobility allows the dimerization equilibrium to respond to thermodynamic control. Above this temperature the dimerization equilibrium is dynamic, *i.e.*, while the fraction of groups associated is specified by temperature, the identity of individual partners is lost. This means that interchange loss mechanisms are present at all temperatures above T_β. This view differs somewhat from that of McKnight, *et al.*[9] Additional evidence will be presented in a subsequent publication.

Conclusions

Three major conclusions may be drawn from the various experimental results.

The first is that the hydrogen bonding dimer formation is thermally reversible above room temperature, and probably above T_g. The thermodynamic parameters of the dimerization, namely, a ΔH of -11.5 kcal/mol and a ΔS of ~ -12 eu per H bond, are almost identical with the values for small molecule acids in nonpolar monomeric solvents. In addition, the monomer–dimer equilibrium is continuous through the melting temperature, implying that the bonding does not occur within crystalline regions. The application of Flory's equation confirms that the dimer formation occurs in the amorphous phase exclusively. These materials are good examples of severely restricted crystallization, showing an inability to generate sizable structures from solution or in bulk.

Within the amorphous phase, the presence of the dimers results in an increase of T_g. The dependence of T_g on acid content is more satisfactorily described by cross-linking equations than by comonomer equations.

Finally, under stress, where an all-*trans* backbone configuration is even more highly favored than at rest, the carboxylic acid side group is not allowed to undergo free rotation, and the dimers tend to lie perpendicular to the direction of stretch.

Acknowledgments. We wish to thank J. P. Luongo and B. Wargotz for their determination of methyl groups and acid content, respectively.

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p,p'-Biphenol–Dianilinosilane Condensation Copolymers[1]

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ABSTRACT: A series of linear polyaryloxysilanes having various combinations of methyl, phenyl, vinyl, and allyl substituents was synthesized by melt-condensing p,p'-biphenol and dianilinosilanes. These soluble thermoplastics were processable and exhibited potentially useful engineering properties at ambient temperature, but softened or fused at undesirable low temperatures, generally below about 100°. Cross-linked, insoluble polymers that softened, but did not melt, at 300° were obtained by free-radical cures of polyaryloxysilanes having pendent vinyl or allyl groups.

A wide variety of polymers based upon modified polysiloxane chains have been explored in recent years. Among these interesting new polymer types are the double-chain phenyl-T polymers,[2] the polysilazanes having silicon–nitrogen linkages,[3] polysilphenylenes in which silicon atoms are linked through phenylene

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[1] Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1965.

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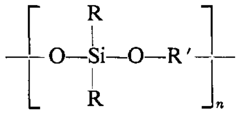
[3] (a) E. G. Rochow and R. Minne, *ibid.*, 82, 5625 (1960); (b) L. W. Breed, R. L. Elliot, and A. F. Ferris, *J. Org. Chem.*, 27, 1114 (1962).

TABLE I
CHARACTERIZATION OF SILANE MONOMERS

Structure	Mp, °C	Bp, °C (mm)	Calcd,[a] % C	Calcd,[a] % H	Calcd,[a] % N	Found,[a] % C	Found,[a] % H	Found,[a] % N
$(C_6H_5NH)_2(C_6H_5)_2$	166–167	...	78.65	4.95	7.66	78.79	5.23	7.92
$(C_6H_5NH)_2Si(CH_3)_2$	63.0–63.5	153.5 (1.1)	69.36	7.49	11.56	69.10	7.55	11.49
$(C_6H_5NH)_2Si(CH_3)(CH{=}CH_2)$	...	160.8–161.3 (1.4)	70.82	7.13	11.02	70.69	7.23	10.88
$(C_6H_5NH)_2(CH_3)(CH_2CH{=}CH_2)$	...	146.0–148.3 (0.5)	71.59	7.51	10.44	71.64	7.74	10.61

[a] Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

units,[4,5] and the polyaryloxysilanes having silicon–oxygen–carbon linkages in their backbones and the general formula



$$\left[-O-\overset{R}{\underset{R}{Si}}-O-R'-\right]_n$$

The preparation and certain structure–property relationships of a number of polyaryloxysilanes have been reported previously.[6-9] The present work concerns polyaryloxysilanes in which R′ is 4,4′-biphenyl, and R is a phenyl, methyl, vinyl, or allyl group, or combinations of these groups. Each of the polymers was synthesized by melt-polymerizing the appropriate dianilinosilane monomer or mixture of dianilinosilane monomers with *p,p*′-biphenol, with aniline being evolved as the polycondensation side product.

$$(C_6H_5NH)_2SiR_2 + HO—R'—OH \rightarrow$$
$$-\!\!\left[O—Si(R_2)—O—R'\right]\!\!-_n + C_6H_5NH_2\uparrow \quad (1)$$

Monomers

The dianilinosilane monomers used (Table I) were prepared by condensing distilled, high-purity dichlorosilanes with aniline in the presence of excess 2,4,6-trimethylpyridine (acid acceptor), a modification of the procedures of Anderson,[10] Curry and Byrd,[7] and Larsson and Smith.[11] This procedure provided dianilinosilanes in yields as high as 90%. The monomers were isolated in highly pure forms by crystallization or distillation.

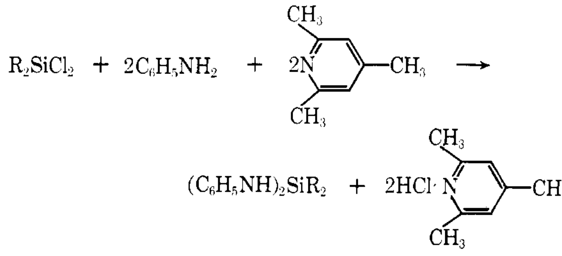


TABLE II
CONDENSATIONS OF DIANILINODIMETHYLSILANE WITH *p,p*′-BIPHENOL

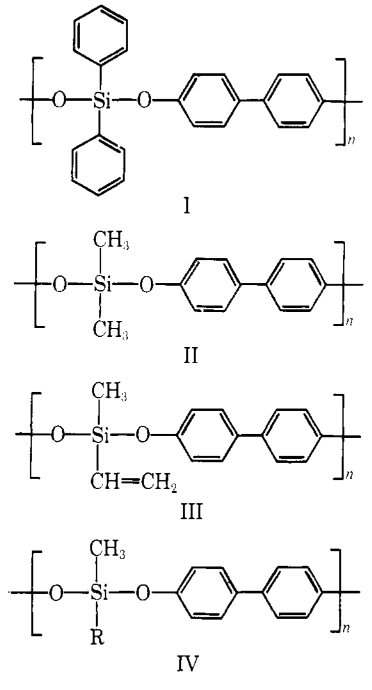
Experiment no.	Polymerization time (hr) at 225° (0.3 mm)[a]	$\overline{M}_w$[b]
1	1.0	8.2×10^4
2	2.0	8.8×10^4
3	3.0	8.6×10^4
4	4.5	9.6×10^4

[a] Following heating for 0.5 hr under nitrogen at 225°. [b] These and other molecular weight values are based on gel permeation chromatography and light scattering data.

Polymer Preparations

The silane monomers were melt-condensed with *p,p*′-biphenol to produce four basic polyaryloxysilane types (Chart I). Equimolar mixtures of the dianilinosilanes and *p,p*′-biphenol were placed in reaction vessels ranging in size from 50-ml polymerization tubes to 500-ml flasks equipped with liquid take-offs, a means for sweeping the system with dry nitrogen, and a vacuum source. The intimately mixed monomers were heated under nitrogen until homogeneous melts were obtained

CHART I



R = part methyl, part vinyl, or allyl

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(4) R. L. Merker, U. S. Patent 3,202,634 (1965).

(5) M. Sveda, U. S. Patent 2,562,000 (1951).

(6) W. R. Dunnavant, R. A. Markle, P. B. Stickney, J. E. Curry, and J. D. Bryd, *J. Polym. Sci.*, **5**, 707 (1967).

(7) J. E. Curry and J. D. Byrd, *J. Appl. Polym. Sci.*, **9**, 295 (1965).

(8) W. R. Dunnavant, R. A. Markle, R. G. Sinclair, P. B. Stickney, J. E. Curry, and J. D. Byrd, *Polym. Preprints*, **8**, 1163 (1967).

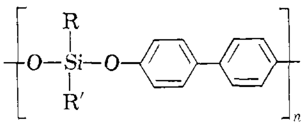
(9) W. R. Dunnavant, R. A. Markle, W. O. Chase, D. A. Berry, P. B. Stickney, J. E. Curry, and J. D. Byrd, *ibid.*, **6**, 1131 (1965).

(10) H. W. Anderson, *J. Amer. Chem. Soc.*, **73**, 5802 (1951).

(11) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

TABLE III

REPRESENTATIVE ELEMENTAL ANALYSIS OF TYPE OF POLYMERS



Polymer type	R	R'	Calcd, % C	Calcd, % H	Found, % C	Found, % H
I	C_6H_5	C_6H_5	78.65	4.95	78.13	4.94
II	CH_3	CH_3	69.39	5.82	69.52	6.03
III	CH_3	$CH_2{=}CH$	70.84	5.55	70.61	5.58
IV	CH_3 (75%)	$CH_2{=}CH$ (25%)	69.75	5.75	69.62	5.68

and aniline refluxed freely. The polymerizations were then completed under a vacuum at temperatures ranging from 200 to 225°. Once initiated, the polymerizations proceeded rapidly and the molecular weights of the polymers obtained were largely a function of monomer purity, and not of polymerization time (Table II), or rate of aniline removal.

The evaluation studies described in this paper were based on polymers as obtained from the melt polymerizations, with no subsequent purification. Typical elemental procedure are shown in Table III and are in good agreement with the calculated values.

General Polymer Properties

The linear polymers of types I–IV were transparent and light yellow to amber. They ranged from hard, brittle glasses to tough, flexible materials depending upon their molecular weights. In general, the polymers had softening temperatures below about 100°. Each of the polymers was self-extinguishing when ignited, and was soluble in such common solvents as benzene, toluene, various chlorobenzenes, and tetrahydrofuran. All of the polymers exhibited typical thermoplastic properties—could be injection-molded at moderate temperatures and pressures, drawn into fibers from their melts, or cast from solutions to form films. Representative properties obtained with polymer I specimens ranging in M_w values from 4.9×10^4 to 8.4×10^4 are shown in Table IV.

The replacement of the phenyl substituents of polymer I by methyl or vinyl groups resulted in polymers having lower softening temperatures and greatly enhanced extensibilities at room temperature. A typical polymer II specimens ($M_w = 4.8 \times 10^4$) was readily converted into transparent, nearly colorless, tough film by solvent casting from *o*-dichlorobenzene, or tough flexible sheet by compression molding. This polymer softened at 85–90° and melted (fibers could be drawn) at 144° when progressively heated at 4°/min on a Fisher-Johns melting point block. The polymer II sheet and film specimens showed up to 150% elongations at break and tensile strengths up to 4700 psi at 25°.

Fibers drawn from a melt of the above polymer II specimen were cold-drawn 130–150% of their original lengths and demonstrated tensile strengths as high as 50,000 psi (tenacities exceeding 4 g/denier). Cold-drawn fibers from a higher molecular weight ($M_w = 9.6 \times 10^4$) sample of polymer II had comparable tenacities. Immersion of polymer II fibers in distilled water at 25° for 14 days did not detectably alter their tensile strengths. X-Ray diffraction patterns obtained for a variety of polymer II samples were all characteristic of amorphous polymers.

TABLE IV

REPRESENTATIVE PROPERTIES OF EXPERIMENTAL POLYMER I SPECIMENS

Tensile strength, psi $\times 10^3$	3.0–8.0
Flexural strength, psi $\times 10^3$	3.1–10.5
Heat deflection temperature, °C (264 psi)	95–108
Per cent elongation at break	5
Impact strength, notched izod, ft-lb/in. of notch	0.15–0.47
Dielectric constant (frequency = 1 mc)	2.84–3.02
Dissipation factor (frequency = 1 mc)	0.0011–0.0014
Dielectric strength, volts/mil (500 V/sec)	513–577

A polymer III specimen ($M_w = 2.9 \times 10^4$) was cast from *o*-dichlorobenzene to form clear, transparent films that softened at 48° and melted at 78°. The casting solution was observed to gel after several days exposure to air, suggesting a ready tendency of polymer III to cross-link. Fibers drawn from a polymer III melt and having diameters ranging from 4.5 to 10 mils had tenacities of 0.46–0.92 g/denier.

Polymer IV samples prepared by condensing mixtures of dianilinodimethylsilane and dianilinomethylvinylsilane with *p,p'*-biphenol were generally similar to polymers II and III. A polymer IV specimen (75% dimethylsilyl and 25% methylvinylsilyl group content) having a weight-average molecular weight of 3.3×10^4 had a softening temperature of 85–90°, could be solvent-cast into tough films, or drawn into fibers (cold-drawable) from its melt. Fiber specimens had tensile strengths up to 26,000 psi (tenacities up to 1.9 g/denier). The mechanical properties of the allyl-substituted polymers were not determined, but appear to be qualitatively similar to those of the analogous vinyl-substituted polyaryloxysilanes.

Programmed Thermogravimetric Analyses

Typical programmed thermogravimetric analyses of polymer types I–IV under nitrogen or a vacuum fell within the boundary curves shown in Figure 1. These thermograms, obtained using a heating rate of 4°/min, indicated weight losses of 5% or less below 400°, the major weight losses occurring above 500° with appreciable polymer residues remaining up to 800°.

Programmed thermogravimetric analyses of polymers

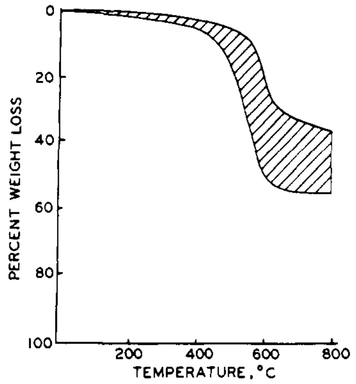


Figure 1. Programmed thermogravimetric analyses of polymers I, II, III, and IV under nitrogen or a vacuum (heating rate of 4°/min). Shaded area includes curves for the four different polymer types.

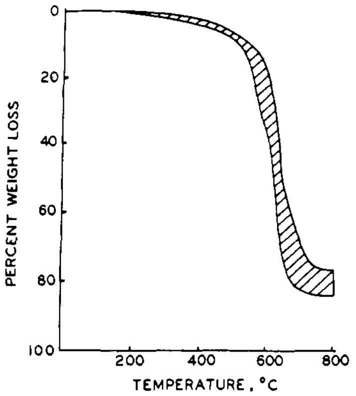


Figure 2. Programmed thermogravimetric analyses of polymers I, II, III, and IV under air (heating rate of 4°/min). Shaded area includes curves for the four different polymer types.

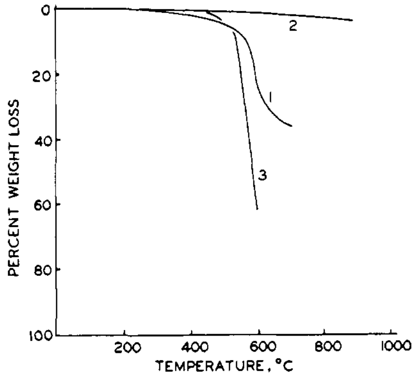


Figure 3. Programmed thermogravimetric analyses of polymer I heated in nitrogen (curve 1), then cooled and reheated in nitrogen (curve 2), or cooled and reheated in air (curve 3).

I–IV under dry air are shown in Figure 2. As in the absence of air, only small weight losses occurred below 400°. However, the decompositions under air were more catastrophic and the polymers were reduced essentially to silica residues at about 700°. The programmed thermogravimetric analyses of these and a variety of other polyaryloxysilanes examined indicated relatively small differences between the stabilities of aromatic and alkyl- or alkenyl-substituted polymer.

In general, the maximum temperatures at which polymers remain stable fall appreciably below the breakdown temperatures indicated by programmed thermogravimetric analyses. In the case of the polyaryloxysilanes, the thermal decompositions appear to occur at significant rates above about 225°, while hydrolytic instability can be encountered at either ambient or elevated temperatures.

Cross-Linking

Polymer I did not undergo cross-linking by free-radical catalysis and has no functional groups through which it can readily be cured using condensation-type reactions. However, earlier polymerization studies[6,7] indicated that polymer I could be obtained in a cross-linked form if its preparation was conducted at 250–300°. When a soluble, fusible polymer I specimen was heated for 24 hr under vacuum at 250°, it underwent a 21% weight loss and was converted into a very hard, insoluble residue. The residue did not soften at 300°. Infrared analysis of the residue indication absorption at 1125–1025 cm^{-1} characteristic of Si–O–Si linkages not present in the spectrum of the unpyrolyzed polymer. A sublimate corresponding to 12% of the initial polymer weight was collected from the walls of the pyrolysis tube and identified as *p*,*p*′-biphenol. Analysis of the head space in the pyrolysis tube by gas chromatography and mass spectrometry revealed the presence of benzene. These results suggest that both silicon–phenyl and silicon–oxygen cleavages occurred during the pyrolysis.

The residues of pyrolyzed polymer I contain a high proportion of the organic contents of the original polymers. These residues have greatly increased thermal stability, but not thermal-oxidative stability as compared to unpyrolyzed polymer I. Thus, a sample of polymer I (M_w = 8.4 × 10^4) was heated to 750° in nitrogen on a thermobalance (curve 1, Figure 3) and a typical 36% weight loss resulted. Upon being cooled, then reheated to 900° in nitrogen, the sample showed only a 3.6% ultimate weight loss (curve 2, Figure 3). A second sample of polymer I was heated to 750° in nitrogen, cooled, then reheated at 4°/min under air. Decomposition began at about 450° and a 60% weight loss was incurred up to 600° (curve 3, Figure 3). The residue's stability under air was essentially identical with that shown by a thermogravimetric analysis of unpyrolyzed polymer I in air (Figure 2).

Despite the fact that polymer II is structurally similar to polydimethylsiloxanes, it was not found to respond to free-radical catalysis to provide cross-linked resins. For example, polymer II films containing 5 wt % benzoyl peroxide or *t*-butyl perbenzoate heated at 100 and 200°, respectively, for 1 hr remained completely fusible and soluble in 1,2,4-trichlorobenzene. Polymer II specimens milled with three parts of dicumyl peroxide, then heated for 2 hr in a closed mold at 160°, also remained soluble and fusible. However, polymers of types III and IV having pendent vinyl groups were found to cross-link when heated with conventional free-radical initiators. Polymer III specimens were converted into insoluble and infusible (at temperatures as high as 370°) materials by heating them with 1–2% of *t*-butyl perbenzoate at 115°.

TABLE V
EFFECT OF PEROXIDE CURES OF UNSATURATED POLYARYLOXYSILANES DERIVED FROM *p,p'*-BIPHENOL

Silyl units (%)		Approximate polymer softening temp, °C	Solubility in benzene
$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-}}$ (50)	$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH{=}CH_2}}{-\mathrm{Si}-}}$ (50)	50–55[a] Nonfusible at 300°[b]	+ –
$\overset{\mathrm{C_6H_5}}{\underset{\mathrm{C_6H_5}}{-\mathrm{Si}-}}$ (50)	$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2{-}CH{=}CH_2}}{-\mathrm{Si}-}}$ (50)	85–90[a] Nonfusible at 300°[b]	+ –
$\overset{\mathrm{C_6H_5}}{\underset{\mathrm{C_6H_5}}{-\mathrm{Si}-}}$ (50)	$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH{=}CH_2}}{-\mathrm{Si}-}}$ (50)	85–90[a] Nonfusible at 300°[b]	+ –
$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-}}$ (50)	$\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2{-}CH{=}CH_2}}{-\mathrm{Si}-}}$ (50)	55–60[a] Nonfusible at 300°[b]	+ –

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

Like polymer I, cross-linked polymer III pyrolyzed under an inert atmosphere provided residues whose infrared spectra showed absorptions (1125–1025 cm^{-1}) characteristic of Si–O–Si linkages not present in the spectrum of the unpyrolyzed polymer, and *p,p'*-biphenol as a sublimate. These findings, together with elemental analyses of the residue, substantiate the fact that significant degrees of chain scission occur during the pyrolysis of polymer III.

Polymer IV films (containing 50% methylvinylsilyl units and 50% dimethylsilyl units), both with and without 5% *t*-butyl perbenzoate, were heated for 1 hr at 160°. The film without catalyst softened at 73°, melted at 121°, and was completely soluble in *o*-dichlorobenzene. The catalyst-containing film swelled but did not dissolve in *o*-dichlorobenzene. It softened at 75°, but did not melt at 220°.

The results of some cross-linking studies involving polymers containing methylvinyl- or methylallylsilyl units are shown in Table V. Four modified type I and type II polymers, having half of their original dimethyl- or diphenylsilyl units replaced by methylvinyl- or methylallylsilyl units, were prepared. These four polymers were highly soluble in benzene and began to soften or melt at temperatures ranging from about 50 to 90° as determined on a melting point block. Each polymer was milled for several minutes at about 100° with three parts of dicumyl peroxide. They were then pressed into 20-mil sheets and cured for 2 hr at 165°. In each case the cured specimens were tough and flexible but insoluble in hot benzene and infusible at 300°. Each of the cross-linked samples softened at about the same temperature as did its uncross-linked form but was rubber- or leatherlike at 300°.

Short-term isothermal weight losses at 200 and 300° for the cross-linked and uncross-linked unsaturated polyaryloxysilanes as well as uncross-linked, soluble polymers I and II are shown in Table VI. A 1-in., 20-mil sheet specimen of each polymer was heated at 300° for 21 hr in a circulating air oven. The specimens showed final weight retentions ranging from 85 to 97%. After aging in air at 300°, all ten of the specimens, including the six previously uncross-linked ones, were insoluble in benzene and failed to fuse at 300°. Each aged specimen had become discolored and brittle.

Duplicate specimens were heated for 21 hr at 200° in air. Several of these samples underwent greater weight losses at 200° than at 300°. In spite of the significant weight losses, each of the ten polymers qualitatively retained a large part of its original strength and flexibility. The four initially uncross-linked specimens underwent varying degrees of cross-linking during the 200° exposure in air. The two allyl-substituted polymers were only partially soluble. After 21 hr at 200° in air, both polymers I and II qualitatively retained most of their original strengths but, unlike the unsaturated polymers, were still fusible and completely soluble in benzene.

Conclusions

This and earlier studies[6–9] indicate that polymers of the polyaryloxysilane type can readily be prepared as high-molecular weight materials, and that such polymers can possess potentially useful engineering properties. However, the polymer types discussed here are known to be sensitive, to varying degrees, to moisture. When exposed to boiling water, they can undergo reductions in molecular weight. They can embrittle slowly when exposed to atmospheric moisture for a number of months. During thermal analyses they undergo more rapid and extensive weight losses at lower temperatures in wet as compared to dry nitrogen.

During syntheses the polyaryloxysilanes can be heated at 200–225° for prolonged periods of time with-

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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Received December 19, 1967

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.

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