

Thermogravimetry and Differential Scanning Calorimetry of Some Poly-*p*-xylylenes Containing Halogen Atoms

B. L. JOESTEN, *Union Carbide Corporation, Chemicals & Plastics Division,
Bound Brook, New Jersey 08805*

Synopsis

Poly-*p*-xylylene and three halogen-containing poly-*p*-xylylenes prepared by the Gorham method from purified dimers were characterized by thermogravimetry and differential scanning calorimetry to determine their relative thermal stabilities in nitrogen and air. As judged by these techniques, thermal stability in nitrogen is not greatly changed by halogenation of the cyclic dimer from which polymer is made. However, thermal oxidative stability depends on the type and degree of halogenation. Aliphatic fluorine atoms greatly improved upon the thermal oxidative stability of poly-*p*-xylylene. To a lesser but significant degree, two aromatic chlorine atoms, poly(dichloro-*p*-xylylene), also improved upon the thermal oxidative stability of poly-*p*-xylylene or poly(chloro-*p*-xylylene). Oxidative degradation caused a rapid exothermic weight loss near 300°C for poly(dichloro-*p*-xylylene) and near 250°C for poly-*p*-xylylene and poly(chloro-*p*-xylylene) when films were heated at 10°C/min. Poly(dichloro-*p*-xylylene) maintained a constant weight during an induction period before it started to lose weight when it was heated isothermally at temperatures below 300°C. However, poly-*p*-xylylene and poly(chloro-*p*-xylylene) gained weight during oxidation before they lost weight when heated isothermally below 250°C.

INTRODUCTION

This paper describes the thermal stability and thermal oxidative stability of some poly-*p*-xylylenes containing aliphatic and aromatic halogen atoms. Prior to the development of the pyrolytic vapor deposition process (Gorham method) for preparing linear poly-*p*-xylylene, halogen-containing poly-*p*-xylylenes could not be easily synthesized. Therefore, their thermal stability in inert or oxidative environments has not received any attention in the literature, even though several workers have described the stability of poly-*p*-xylylene.¹⁻¹⁰

The Gorham method for making poly-*p*-xylylene is based on the vacuum pyrolysis of cyclic di-*p*-xylylene (DPX) near 600°C followed by vapor deposition polymerization of *p*-xylylene below 30°C.¹¹ The synthesis of cyclic dimer containing predominantly two or four chlorine atoms was described by Gorham and Yeh.¹² The synthesis of cyclic dimer with fluorine atoms substituted for each of the aliphatic hydrogen atoms was described by Chow, Pilato, and Wheelwright.¹³ Corresponding polymers

TABLE I
Halogen-Containing Poly-*p*-xylylenes

Polymer	Parylene designation*
$\left(\begin{array}{c} \text{H} & & \text{H} \\ & & \\ -\text{C} & \text{---} & \text{C} \\ & & \\ \text{H} & & \text{H} \end{array} \right)_n$	N
$\left(\begin{array}{c} \text{H} & \text{Cl} & \text{H} \\ & & \\ -\text{C} & \text{---} & \text{C} \\ & & \\ \text{H} & & \text{H} \end{array} \right)_n$	C
$\left(\begin{array}{c} \text{H} & \text{Cl} & \text{H} \\ & & \\ -\text{C} & \text{---} & \text{C} \\ & & \\ \text{H} & & \text{H} \\ & \text{Cl} & \end{array} \right)_n$	D
$\left(\begin{array}{c} \text{F} & & \text{F} \\ & & \\ -\text{C} & \text{---} & \text{C} \\ & & \\ \text{F} & & \text{F} \end{array} \right)_n$	AF-4

* Parylene is the generic name given to the family of poly-*p*-xylylenes prepared by the Gorham method. N, C, and D are presently marketed by Union Carbide Corporation. AF-4 is not commercially available.

have been prepared from the halogen-containing dimers.¹⁴ The structure and nomenclature of these polymers are shown in Table I.

The polymer films were characterized by thermogravimetry (TG) to determine their relative thermal stabilities in nitrogen and their relative thermal oxidative stabilities in air. Parylene C and parylene D were also characterized by differential scanning calorimetry to compare the enthalpic changes associated with their thermal oxidative degradation. The polymer films were made from cyclic dimers that were recrystallized twice from solution. Following polymerization, the films were extracted in methylene chloride at 35–40°C for 4 hr to remove any residual unreacted DPX materials. The films were then vacuum dried at 100–110°C to remove the solvent.

RESULTS AND DISCUSSION

Figure 1 shows thermogravimetric curves for parylene N when it is heated in nitrogen or air. The weight is stable in nitrogen until the temperature approaches 450°C. Near 450°C, the weight decreases very rapidly to a residual weight of approximately 10% at 500°C. The thermogravimetric data in nitrogen agree with the observations of Madorsky and Straus⁵ and of Jellinek and Lipovac⁹ who found that the rate of weight loss of poly-*p*-xylylene in vacuum is not significant below 400°C. Jellinek and Lipovac observed a decrease in reduced viscosity when poly-*p*-xylylene film was

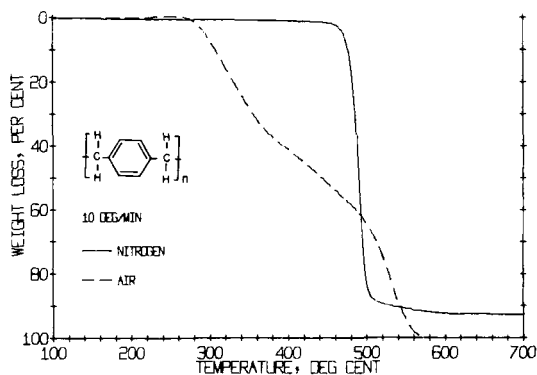


Fig. 1. Thermogravimetry of poly-*p*-xylylene at 10°C/min.

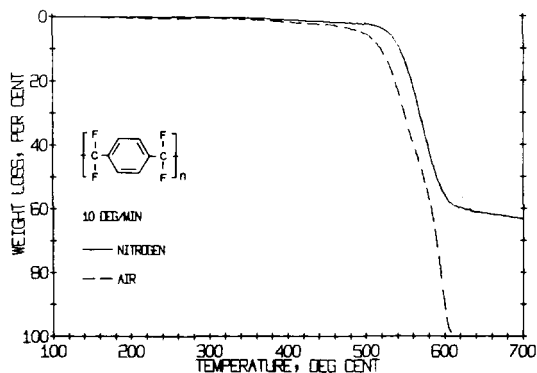


Fig. 2. Thermogravimetry of poly(tetrafluoro-*p*-xylylene) at 10°C/min.

heated in vacuum at 424°C for 2 min.⁹ Therefore, the thermal degradation is apparently initiated by random chain scission.

The weight of parylene N is considerably less stable in air than in nitrogen as a result of oxidative degradation. The weight increases slightly to a maximum value near 270°C and then decreases rapidly—about 180°C sooner than in nitrogen. The weight gain suggests the formation of peroxy radicals.

Figure 2 shows the thermogravimetric data for parylene AF-4 when it is heated in nitrogen or air. Parylene AF-4 does not lose weight catastrophically in nitrogen until 530°C, i.e., 80°C higher than the corresponding temperature for parylene N.

When heated in air, the weight of parylene AF-4 does not decrease catastrophically until 500°C, only 30°C below the temperature where it occurs in nitrogen and about 230°C higher than where it occurs for parylene N in air. Furthermore, parylene AF-4 does not gain a detectable amount of weight prior to catastrophic weight loss. Based on the similarity of the thermogravimetric data in air to those in nitrogen over the first 60% of the weight loss, oxidative pyrolysis of parylene AF-4 apparently involves the

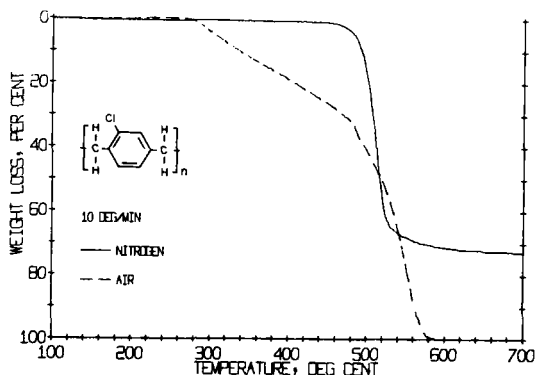


Fig. 3. Thermogravimetry of poly(chloro-*p*-xylylene) at 10°C/min.

process that occurs in nitrogen followed by the oxidation of the residual carbonaceous char. The similarity between the behavior in air and in nitrogen suggests that parylene AF-4 has very good oxidative stability. This is, in fact, the case. Chow, Loeb, and White¹⁴ found that parylene AF-4 retained useful mechanical and electrical properties after 3000 hr at 250°C in air. The good thermal oxidative stability of parylene AF-4 most likely results from the high stability of the C-F bond and provides some evidence that oxidative attack starts at the aliphatic C-H bonds in parylene N.

Thermogravimetric data for parylene C are shown in Figure 3. In nitrogen, the weight is stable until 450°C just as for parylene N. Apparently, the single aromatic chlorine atom does not change the strength of the bond at which the random chain scission occurs. However, the weight does not decrease as rapidly for parylene C as for parylene N, and the residue at 600°C is greater for parylene C than for parylene N; so the propagation and/or the termination of the degradation reactions are apparently affected by the chlorine atom.

The initial effects of oxidative degradation on the thermogravimetric data are very similar for parylene C and parylene N. Parylene C gains weight in air and attains a maximum value near 270°C. So substitution of a chlorine atom for one of the aromatic hydrogen atoms does not noticeably affect the formation of peroxy radicals. The subsequent weight loss is not as rapid for parylene C as for parylene N.

Figure 4 shows differential scanning calorimetry data for parylene C when heated in nitrogen and air. When heated in nitrogen, an endothermic transition appears which peaks near 295°C. If the polymer is cooled at 5°C/min from above the endotherm, an exotherm occurs near 267°C. Subsequent reheating reveals an endotherm near 277°C. The reversible nature of the transition indicates that it is attributable to crystalline melting. Since the endotherm appears sooner on the second heating cycle relative to the first heating cycle, the crystalline phase which forms during polymerization is more perfect than that which forms when the film is

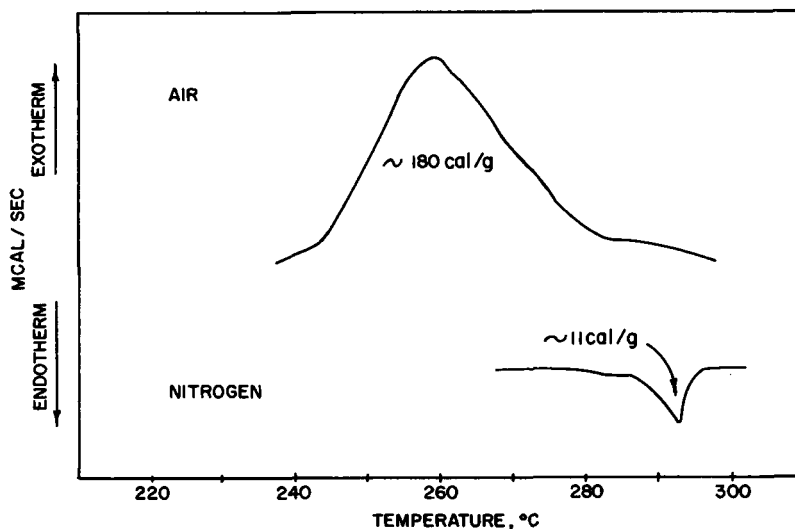


Fig. 4. Differential scanning calorimetry of poly(chloro-*p*-xylylene) at 10°C/min.

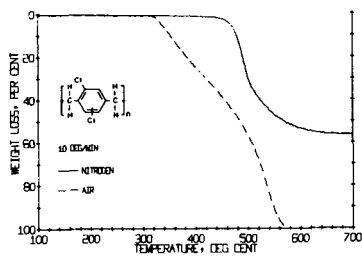


Fig. 5. Thermogravimetry of poly(dichloro-*p*-xylylene) at 10°C/min.

cooled at 5°C/min. Modulus-temperature data for parylene C also indicate a crystalline melting temperature near 295°C.¹⁵

When heated in air, parylene C shows a strong exotherm which starts near the same temperature that an increase in weight was observed. The weight increase is an exothermic process as is expected for the formation of peroxy radicals.¹¹

Figure 5 shows the thermogravimetric data for parylene D. In nitrogen, the behavior of parylene D is similar to that of parylene N or C except for the larger quantity of residue at 700°C.

In air, parylene D behaves quite differently than parylene N or C. First, the weight of parylene D does not increase before it starts to decrease. Second, the onset of rapid weight loss does not occur until 320°C, i.e., 50°C higher than where it occurs in parylene N or C. Therefore, when two chlorine atoms are substituted for two of the aromatic hydrogen atoms, the formation of peroxy radicals is prevented, or, at least kept to undetectably low values. As a result, the formation of volatile fragments is delayed about 50°C.

TABLE II
Measurements of t_m for Parylene N and Parylene C at Constant Temperature

	Time to maximum weight (t_m), min		
	220°C	225°C	250°C
Parylene N	240	30	3.6
Parylene C	120	20	3.6
		21	6.0
			6.6

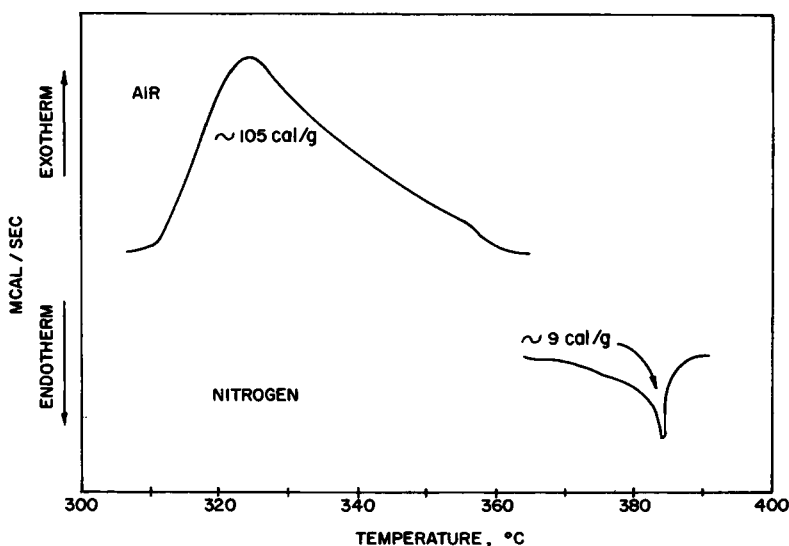


Fig. 6. Differential scanning calorimetry of poly(dichloro-*p*-xylylene) at 10°C/min.

DSC data for parylene D are shown in Figure 6. When heated in nitrogen, parylene D also shows a reversible endothermic transition which is attributed to crystalline melting. However, the crystalline melting temperature of parylene D is about 100°C higher than that of parylene C.

When heated in air, parylene D reveals an exotherm which starts near 320°C, the same temperature where the weight started to decrease rapidly. Therefore, the thermogravimetric data and the calorimetric data both indicate the thermal oxidative stability of parylene D is significantly better than that of parylene C.

The stabilities of parylene C and parylene D were characterized further by measuring their weight at constant temperature near the temperature where rapid weight loss occurred under dynamic conditions. Figure 7 shows typical isothermal data for parylene C and D. Results for parylene N were very similar to those of parylene C. For parylene C, the weight increased slightly, passed through a maximum, and then decreased. The time t_m required for the weight to reach its maximum value decreased with increasing temperature (Table II).

TABLE III
Measurements of Induction Time for Parylene D at Constant Temperature

	Induction time (t_i), min				
	250°C	275°C	280°C	290°C	300°C
By thermogravimetry	180	12			4.2
		30			6.6
					4.2
By differential scanning calorimetry		26	17	9	4.4
		23	17	9	4.8
		23	18		4.8
					4.6
					4.3

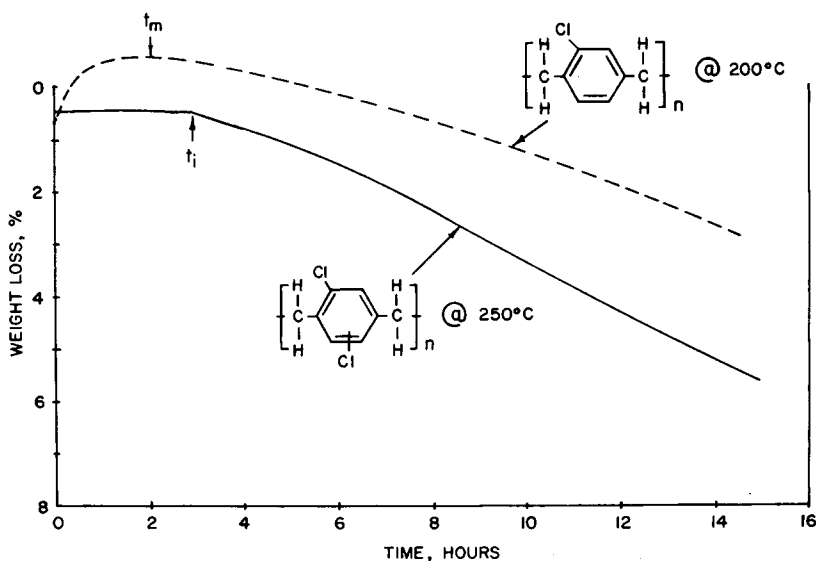


Fig. 7. Thermogravimetry of poly(chloro-*p*-xylylene) and poly(chloro-xylylene) at constant temperature.

For parylene D, the rate of weight loss was comparable to that of parylene C when the temperature was 50°C higher than that of parylene C. The weight of parylene D was constant at each test temperature for an induction period t_i , which decreased as the temperature increased (Table III). The induction period for parylene D could also be measured by differential scanning calorimetry, as illustrated in Figure 8. The induction times obtained by DSC were equal to those obtained by TG (Table III). So the formation of volatile fragments in parylene D occurs simultaneously with the onset of exothermic oxidative reactions.

The measurements of t_i and t_m indicate that parylene D is significantly more stable than parylene C in an oxidative environment at the temperatures where t_i and t_m can be conveniently measured by thermogravimetry.

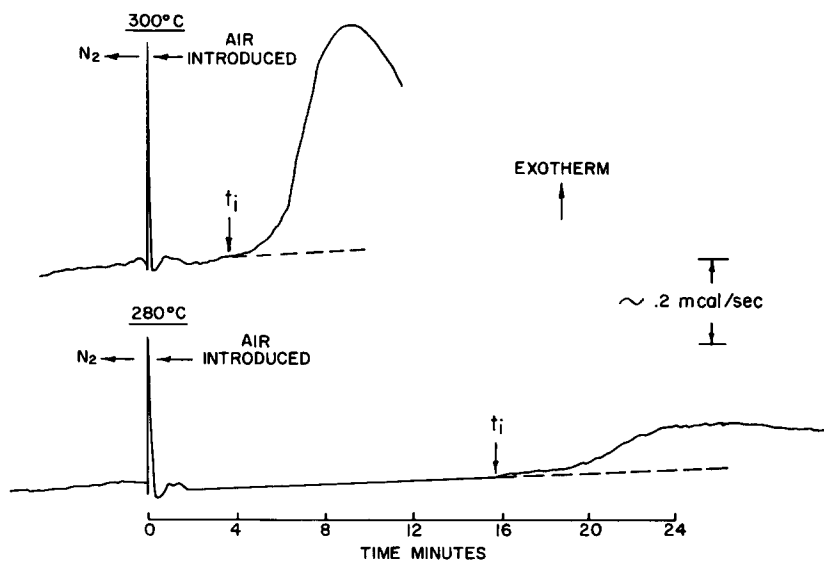


Fig. 8. Differential scanning calorimetry of poly(dichloro-*p*-xylylene) at constant temperature.

Attempts to explain why parylene D has better oxidative stability than parylene N or C would be very speculative until additional characterization is available to support the thermal characterization. Knowledge of the position of the second chlorine atom would help explain its effect on the oxidative stability. While bromination of the cyclic dimer has been characterized, the chlorination of cyclic dimer must still be determined.¹⁶ Mechanical relaxation measurements favor the 2,5- and 2,6-distributions of the two chlorine atoms, but they cannot distinguish between the two possibilities.¹⁷ The 2,5-distribution would place a chlorine atom in close proximity to each CH₂ group in the backbone and provide the greatest possibility for shielding the CH₂ group from oxygen or for stabilizing the C-H bonds by withdrawing electrons.

A determination of what controls the end of the induction period in parylene D would also help explain why it has better oxidative stability than parylene N or C. Even though enthalpic or weight changes were not detected, a dynamic steady state condition most likely exists during the induction period before autocatalytic oxidation occurs.

EXPERIMENTAL

Sample Preparation

The di-*p*-xylylene (DPX) was typical of commercially available dimer. The chlorinated dimers were prepared on commercial equipment. The fluorinated dimer was synthesized in the laboratory. The dimers were recrystallized at least one time as indicated in Table IV. Recrystallization of the tetrachloro-DPX was necessary to remove trichloro-DPX and pentachloro-DPX.

TABLE IV
Solvents Used for Recrystallizing Dimer

Dimer	Solvent
Di- <i>p</i> -xylylene	<i>p</i> -xylene
One chlorine atom on each ring	1st, trichloroethylene 2nd, isopropanol/benzene
Two chlorine atoms on each ring	1st, trichloroethylene 2nd, trichloroethylene
Each aliphatic hydrogen atom replaced with a fluorine atom	hexane

The dimers were polymerized by the Gorham method.¹¹ The polymerized films were removed from the deposition zone and extracted in methylene chloride at 35–40°C for 4 hr to remove any residual unreacted DPX materials. The films were then vacuum dried at 100–110°C to remove the solvent. Infrared analysis of the polymerized films confirmed that the dimers were effectively purified by the recrystallization.

Thermogravimetry

The thermogravimetric data were obtained with a Perkin-Elmer TGS-1 thermobalance. The TGS-1 incorporates a Cahn electrobalance to measure the weight of a sample suspended within a microfurnace with a closed bottom. Either air or nitrogen flowed past the furnace at 30 cc/min. To determine the temperature–time relationship for the microfurnace, a permanent magnet was placed around the microfurnace and a group of magnetic metal alloys that lose their magnetism at well-defined temperatures was heated at a constant rate.¹⁸ The temperature programmer was calibrated for the isothermal experiments by determining the corrections to the magnetic transition temperatures at several heating rates and extrapolating to zero heating rate. For the isothermal experiments, the sample was heated to the test temperature at 160°C/min. The temperature reached the desired value approximately 1 min after the temperature programmer was stopped. The oxidation times reported in the text do not include the heating-up period.

Discs about $\frac{1}{8}$ in. in diameter were cut from the films and stacked in a platinum sample pan. The sample weight was kept as close as possible to 1 mg (3–5 discs) for the dynamic measurements. The sample size was increased to 2 mg for the isothermal measurements so that the instrument sensitivity could be increased twofold.

The TG data were recorded on paper tape using the Perkin-Elmer ADS-VI analytical data system. Programs were written for the IBM 1130 to reduce the data and plot the weight loss versus time or temperature via a Calcomp plotter.

Differential Scanning Calorimetry

Enthalpic changes were measured with a Perkin-Elmer DSC-1B differential scanning calorimeter. The temperature programmer was calibrated with a group of pure metals.

A single disc of film, $\frac{1}{4}$ in. in diameter, was placed in an aluminum pan and covered with a disc of 100-mesh stainless steel screens.¹⁹ The screen ensured that the film was kept in good thermal contact with the bottom of the pan and provided good control over the environment of the film for oxidation experiments.

The sample was heated at 10°C/min for the dynamic measurements. For isothermal experiments, the sample was heated to the desired temperature in nitrogen. When the baseline was established in nitrogen, air was let into the sample chamber at the same flow rate as that of the nitrogen (30 cc/min). After a transient response, caused by the disturbance to the gas flow, the instrument returned to the original baseline. Subsequent oxidation caused an exothermic response.

Mr. D. D. Stewart purified the dimers and made the parylene films used for this study. The TG and DSC data were obtained with the able assistance of Mr. J. P. Zebrowski. The author is grateful for discussions with Drs. W. E. Loeb, M. A. Spivack, and J. F. Gaasch and Messrs. W. D. Niegisch and D. D. Stewart of the Union Carbide Corporation and Prof. D. J. Cram of the University of California at Los Angeles.

References

1. M. Szwarc, *J. Polym. Sci.*, **6**, 319 (1951).
2. R. S. Corley, H. C. Haas, M. W. Kane, and D. I. Livingston, *J. Polym. Sci.*, **13**, 137 (1954).
3. M. H. Kaufman, H. F. Mark, and R. B. Mesrobian, *J. Polym. Sci.*, **13**, 3 (1954).
4. L. A. Auspos, *J. Polym. Sci.*, **15**, 10 (1955).
5. S. L. Madorsky and S. Straus, *J. Res. Nat. Bur. Stand.*, **55**, 223 (1955).
6. J. R. Schaefgen, *J. Polym. Sci.*, **41**, 133 (1959).
7. A. T. Kalashnik, I. Ye. Kardash, T. S. Shpitionova, and A. N. Pravednikov, *Vysokomol. Soyed.*, **8** (3), 526 (1966); *ibid.*, **2B**, 89 (1968).
8. J. M. Lancaster and W. W. Wright, *J. Appl. Polym. Sci.*, **11**, 1641 (1967).
9. H. H. G. Jellinek and S. N. Lipovac, *J. Polym. Sci. A-1*, **8**, 2517 (1970).
10. H. H. G. Jellinek and S. H. Ronel, *J. Polym. Sci. A-1*, **9**, 2605 (1971).
11. W. F. Gorham, *J. Polym. Sci. A-1*, **4**, 3076 (1966); W. F. Gorham (to Union Carbide Corp.), U.S. Pat. 3,342,754 (1967).
12. Y. L. Yeh and W. F. Gorham, *J. Org. Chem.*, **34**, 2366 (1969); W. F. Gorham (to Union Carbide Corp.), U.S. Pat. 3,221,068 (1965).
13. S. W. Chow, L. A. Pilato, and W. L. Wheelwright, *J. Org. Chem.*, **35**, 20 (1970); S. W. Chow (to Union Carbide Corp.), U.S. Pat. 3,268,599 (1966).
14. W. F. Gorham, Advan. Chem. Ser. #91, American Chemical Society, Washington, D.C. 1969; S. W. Chow, W. E. Loeb, and C. E. White, *J. Appl. Polym. Sci.*, **13**, 2325 (1969).
15. W. F. Gorham and W. D. Niegisch, in *Encyclopedia of Polymer Science and Technology*, Vol. 15, H. F. Mark, N. Gaylord, and N. M. Bikales, Eds., Interscience, New York, 1971.
16. H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3527 (1969).
17. C. I. Chung and J. A. Sauer, *J. Polym. Sci. A-2*, **9**, 1097 (1971).
18. S. D. Norem, M. J. O'Neill, and A. P. Gray, *Thermochim. Acta*, **1**, 29 (1970).
19. S. M. Ellerstein, Proceedings of the ACS Symposium on Analytical Calorimetry held in San Francisco, California, April 2-5, 1968, R. S. Porter and J. F. Johnson, Eds., Vol. 1, p. 279.

Received July 19, 1973