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P. M. Hergenrother^{ab}; R. T. Rafter^a; E. S. Harrison^a

^a Polymer Chemistry Department WRD, A Division of Whittaker Corporation, San Diego, California ^b Polymer Section, NASA Langley Research Center, Hampton, Virginia

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Polyphenyl-as-triazines from Perfluoroalkyleneamidrazones*

P. M. HERGENROTHER,[†] R. T. RAFTER, and E. S. HARRISON

Polymer Chemistry Department
WRD, A Division of Whittaker Corporation
San Diego, California 92123

ABSTRACT

High molecular weight polyphenyl-as-triazines were prepared at ambient temperature by the cyclopolycondensation of perfluoroglutarimidrazone and perfluoroadipimidrazone with various bis(1,2-dicarbonyl) monomers. The effect which the perfluoroalkylene group had upon certain chemical and physical properties of the polymers was determined. Thermal evaluation involved TGA, DSC, TMA, and isothermal weight loss studies of films at 232°C in air. The polymers exhibited excellent hydrolytic stability as evidenced by retention of η_{inh} after boiling in water (24 hr) and 10% sodium hydroxide solution (8 hr). A stable uncyclized intermediate was isolated from the reaction of perfluoroadipimidrazone and benzil which was cyclized to the phenyl-as-triazine model compound [3,3'-perfluorotetramethylenedi(5,6-diphenyl-as-triazine)].

INTRODUCTION

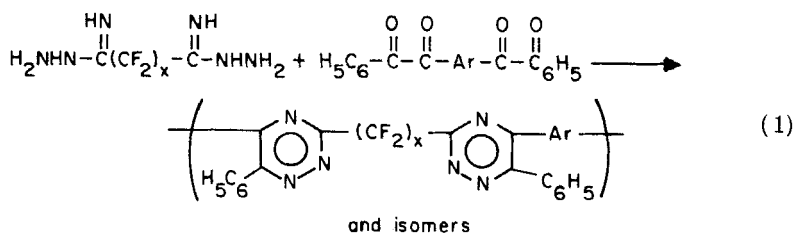
Polyphenyl-as-triazines are soluble high molecular weight high temperature thermoplastics which are potentially useful in functional

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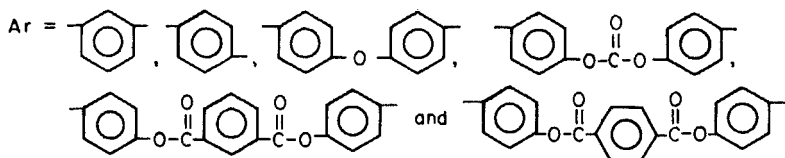
[†]Present address: Polymer Section, NASA Langley Research Center, Hampton, Virginia 23665.

and structural applications demanding high chemical and thermal stability. These polymers were first reported in 1969 [1]. Since then, additional work has been disclosed on their synthesis [2-6], thermal characterization [7], and preliminary mechanical evaluation [2, 3, 8, 9].

The work reported herein involves the preparation of a variety of phenyl-as-triazine polymers from the reaction of two perfluoroalkyleneamidrazones with various bis(1,2-dicarbonyl) monomers (Eq. 1).



where $x = 3$ and 4 .



This work was performed as part of a study to determine the effect of a perfluoroalkylene group upon certain chemical and physical properties of the polymers and to serve as a guide to the future synthesis of highly fluorinated as-triazine polymers.

RESULTS AND DISCUSSION

Monomers

Perfluoroglutaramidrazone and perfluoroadipamidrazone were prepared by the addition of the respective nitrile to hydrazine in isopropyl alcohol at -20°C following a known procedure [10]. After recrystallization from a mixture of isopropyl alcohol and water,

the perfluoroalkyleneamidrazones were obtained as white crystals with the melting points recorded in Table 1. The melting behavior of the perfluoroglutaramidrazone and perfluroadipamidrazone is very dependent upon the heating rate as shown in the differential scanning calorimetric curve in Fig. 1. When a visual melting point was determined on perfluoroglutaramidrazone at a heating rate of $2^{\circ}\text{C}/\text{min}$, the white crystals turned yellow, then reddish-brown, and melted with decomposition at 147 to 148°C . When a sample was heated to 123°C at a heating rate of $2^{\circ}\text{C}/\text{min}$ and held at 123°C for 11 min, it underwent the same color change and melted with decomposition.

The various bis(1,2-dicarbonyl) monomers in Table 1, except for the carbonate monomer, were prepared by known routes as

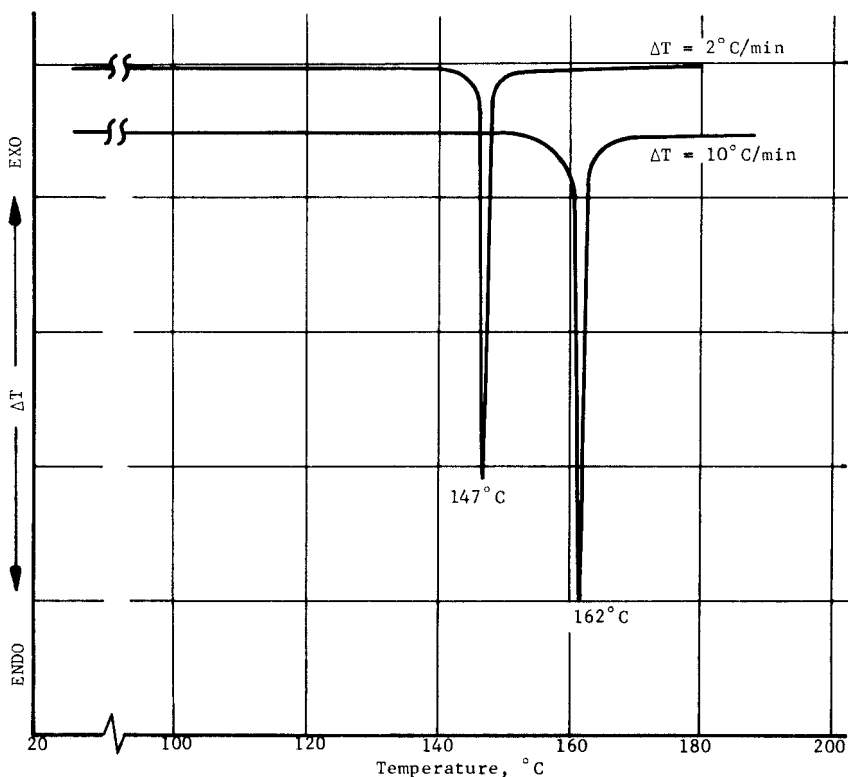
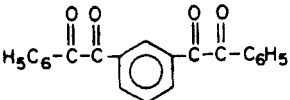
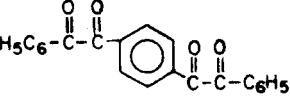
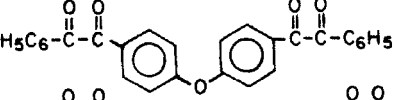
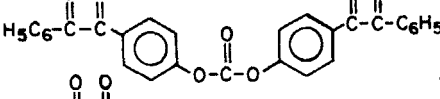
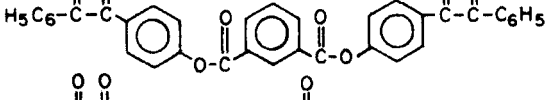
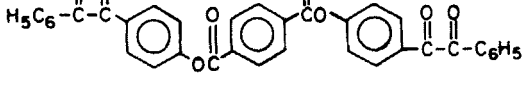


FIG. 1. Differential scanning calorimetric curve of perfluoroglutaramidrazone.

TABLE 1.

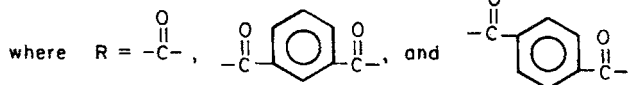
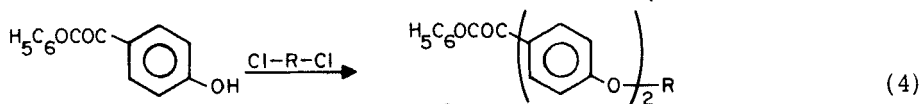
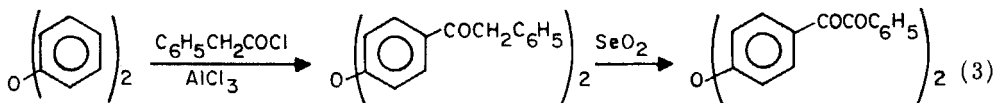
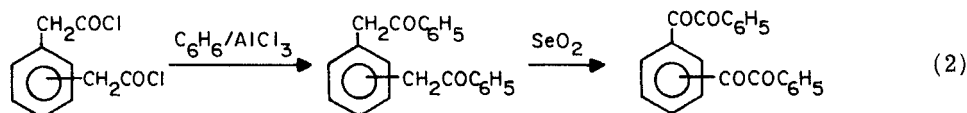
Compound	m_p ($^{\circ}\text{C}$)
$\text{H}_2\text{NHN}-\overset{\text{HN}}{\parallel}{\text{C}}-(\text{CF}_2)_3-\overset{\text{NH}}{\parallel}{\text{C}}-\text{NHNH}_2$	147-148 (dec)
$\text{H}_2\text{NHN}-\overset{\text{HN}}{\parallel}{\text{C}}-(\text{CF}_2)_4-\overset{\text{NH}}{\parallel}{\text{C}}-\text{NHNH}_2$	183-184 (dec)
	98-99
	125-126
	106-107
	159-160
	174-175
	225-226

^aTheoretical values in parenthesis

Monomers

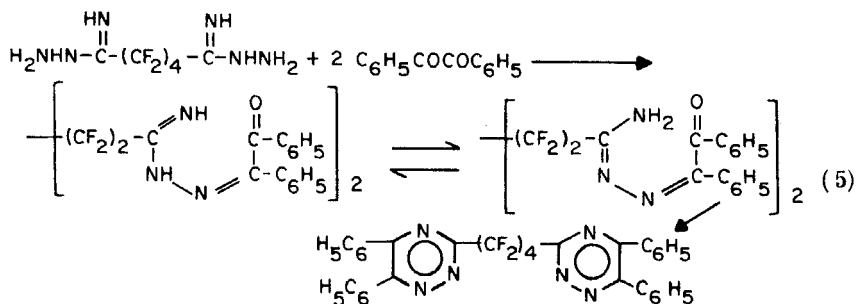
Lit. m_p ($^{\circ}\text{C}$) [Ref]	Formula	Elemental analysis ^a			
		% C	% H	% N	% F
123 (dec) [11] 111-112.5 [10]	$\text{C}_5\text{H}_8\text{N}_6\text{F}_6$	22.67 (22.56)	3.09 (3.03)	31.61 (31.58)	42.72 (42.83)
131 (dec) [11] 175 (dec) [10]	$\text{C}_6\text{H}_8\text{N}_6\text{F}_8$	22.49 (22.79)	2.45 (2.55)	26.57 (26.58)	48.48 (48.07)
98-98.5 [12]	$\text{C}_{22}\text{H}_{14}\text{O}_4$	-	-	-	-
125-126 [13]	$\text{C}_{22}\text{H}_{14}\text{O}_4$	-	-	-	-
106.4-107.4 [14]	$\text{C}_{28}\text{H}_{18}\text{O}_5$	-	-	-	-
-	$\text{C}_{29}\text{H}_{18}\text{O}_7$	73.09 (72.80)	3.83 (3.77)	-	-
173-174 [6]	$\text{C}_{36}\text{H}_{22}\text{O}_8$	-	-	-	-
225-226 [7]	$\text{C}_{36}\text{H}_{22}\text{O}_8$	-	-	-	-

shown in Eqs. (2) to (4). The carbonate containing monomer was prepared from the interfacial reaction of *p*-hydroxybenzil and phosgene.



Model Compounds

Two model compounds were prepared from the reaction of stoichiometric quantities of perfluoroglutaramidrazone and perfluoro adipamidrazone with benzil. The latter yielded a white suspension after stirring in *m*-cresol at ambient temperature for 18 hr. Filtration provided a white solid which was washed with methanol and dried. The IR spectrum (Fig. 2) and elemental analysis (Table 2) of the white solid (30% yield) were consistent with the proposed structure of the uncyclized intermediate in Eq. (5).



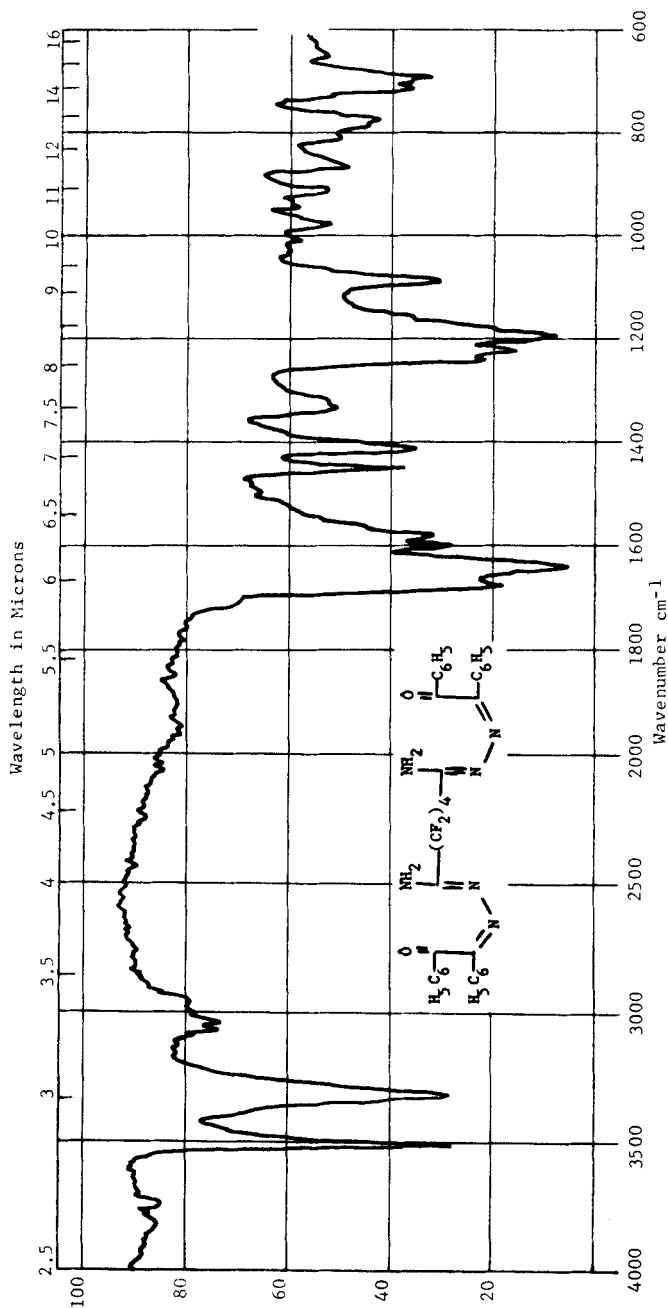


FIG. 2. Infrared spectrum (KBr) of uncyclized intermediate.

TABLE 2. Model Compounds

Compound	Color	mp (°C)	Formula	Elemental analysis ^a			
				% C	% H	% N	% F
$\left[\text{-(CF}_2\text{)}_2 \text{-} \begin{array}{c} \text{NH}_2 \\ \\ \text{C} \\ \\ \text{N} \text{---} \text{N} \text{---} \text{C} \\ \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \text{O} \quad \quad \quad \text{C}_6\text{H}_5 \\ \quad \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \quad \text{C}_6\text{H}_5 \end{array} \right]_2$	White	194.5-195.5 (dec)	C ₃₄ H ₂₄ F ₈ N ₆ O ₂	58.35 (58.28)	3.62 (3.45)	12.02 (11.99)	21.57 (21.69)
$\left[\text{-(CF}_2\text{)}_2 \text{-} \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{N} \text{---} \text{C} \\ \quad \quad \quad \\ \text{N} \quad \quad \quad \text{C}_6\text{H}_5 \end{array} \right]_2$	Yellow	185-186	C ₃₄ H ₂₀ F ₈ N ₆	61.50 (61.44)	3.20 (3.03)	12.62 (12.64)	22.62 (22.87)
$\text{CF}_2 \text{-} \left(\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{N} \text{---} \text{C} \\ \quad \quad \quad \\ \text{N} \quad \quad \quad \text{C}_6\text{H}_5 \end{array} \right)_2$	White	175-176	C ₃₃ H ₂₀ F ₆ N ₆	64.55 (64.49)	3.05 (3.28)	13.55 (13.68)	18.93 (18.55)

^aTheoretical values in parenthesis.

Cyclodehydration to the as-triazine proceeded at a slow rate (several days) in *m*-cresol at ambient temperature, relatively fast (~ 1 hr) in *m*-cresol at 100°C , and very fast (few minutes) in *m*-cresol at 200°C or in a melt at 200°C as evidenced by solubility, melting point, and IR spectroscopic analysis. The IR spectra of the ring-closed model compound, 3,3'-perfluorotetramethylenedi(5,6-diphenyl-as-triazine), is presented in Fig. 3. Characterization of the uncyclized intermediate and the two final model compounds is presented in Table 2.

As anticipated, the reactivity of perfluoroalkyleneamidrazones is significantly reduced relative to other diamidrazones (e.g., oxalamidrazone and 2,6-pyridinediyl diamidrazone) due to the strong inductive effect of the perfluoroalkylene group. The stable uncyclized intermediate appears to be the first such compound isolated in the as-triazine series. No attempt was made to isolate the open-ring intermediate in the perfluorotrimethylene model compound.

Polymers

Polymer synthesis (Eq. 1) was conducted on a 0.1 mole scale in *m*-cresol at 10% solids content (w/v) at ambient temperature. Samples were isolated periodically by precipitation in methanol, washed well with methanol, dried at 80°C in vacuo, and characterized as shown in Table 3. Flexible transparent yellow films (~ 2 mils thick) were cast for all the polymers except for No. 2, with the film from polymer No. 6 exhibiting the least coloration. The film from polymer No. 2 was brittle, apparently due to its low molecular weight ($\eta_{\text{inh}} = 0.42$). However, the film from polymer No. 8 was tough and flexible although the η_{inh} was only 0.39 dl/g. The IR spectra of the polymer films were consistent with those expected for the proposed polymer structures. The IR spectrum of a representative polymer (No. 3, Table 3) is shown in Fig. 4.

As indicated in Table 3, the inherent viscosity (η_{inh}) of the ester- and carbonate-containing polymers decreased upon long-time stirring in *m*-cresol whereas the η_{inh} of the other polymers increased as a function of time. Apparently, *m*-cresol partakes in transesterification with the ester- and carbonate-containing polymers. Additional work is being done to verify this.

The decreased reactivity of perfluoroalkyleneamidrazones is readily apparent when the time required for high molecular weight polymer formation is compared with that from oxalamidrazone or 2,6-pyridinediyl diamidrazone. For example, oxalamidrazone with *p*-bis(phenylglyoxylyl) benzene on a 0.01 mole scale in *m*-cresol at a solids content (w/v) of 10% gave relatively high molecular weight polymer after only 1 hr [3]. Preliminary work has indicated that

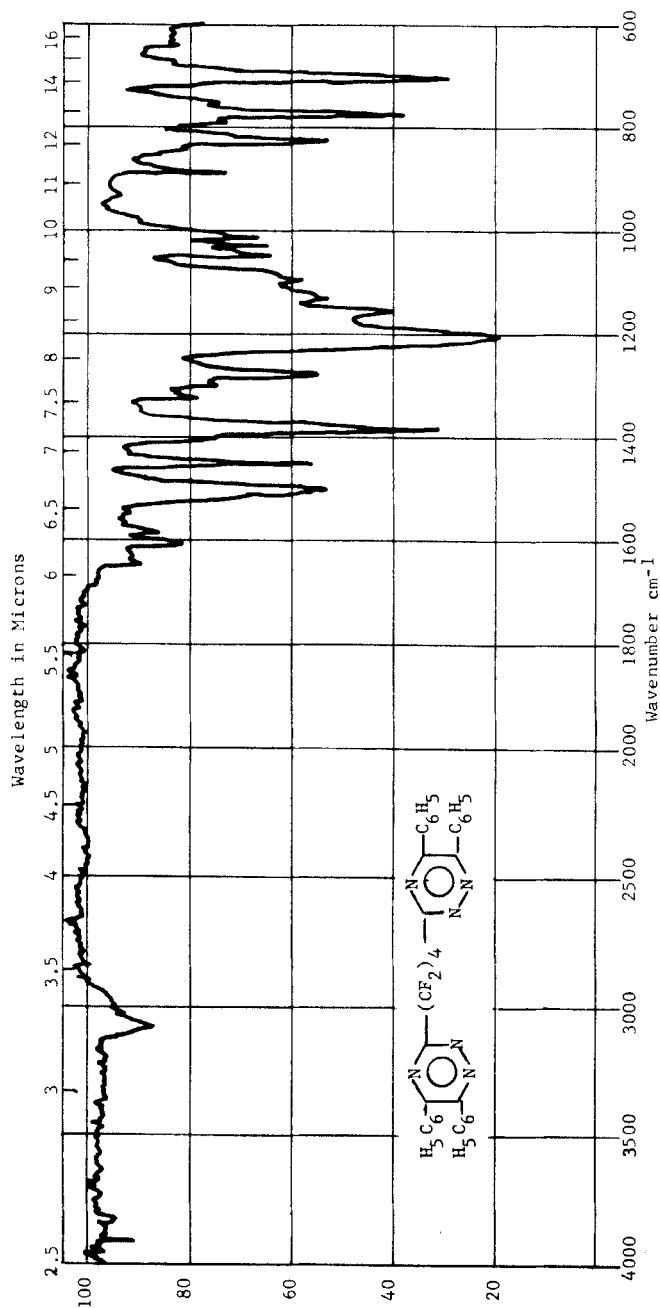


FIG. 3. Infrared spectrum (KBr) of 3,3'-perfluorotetramethylenedi(5,6-diphenyl-as-triazine).

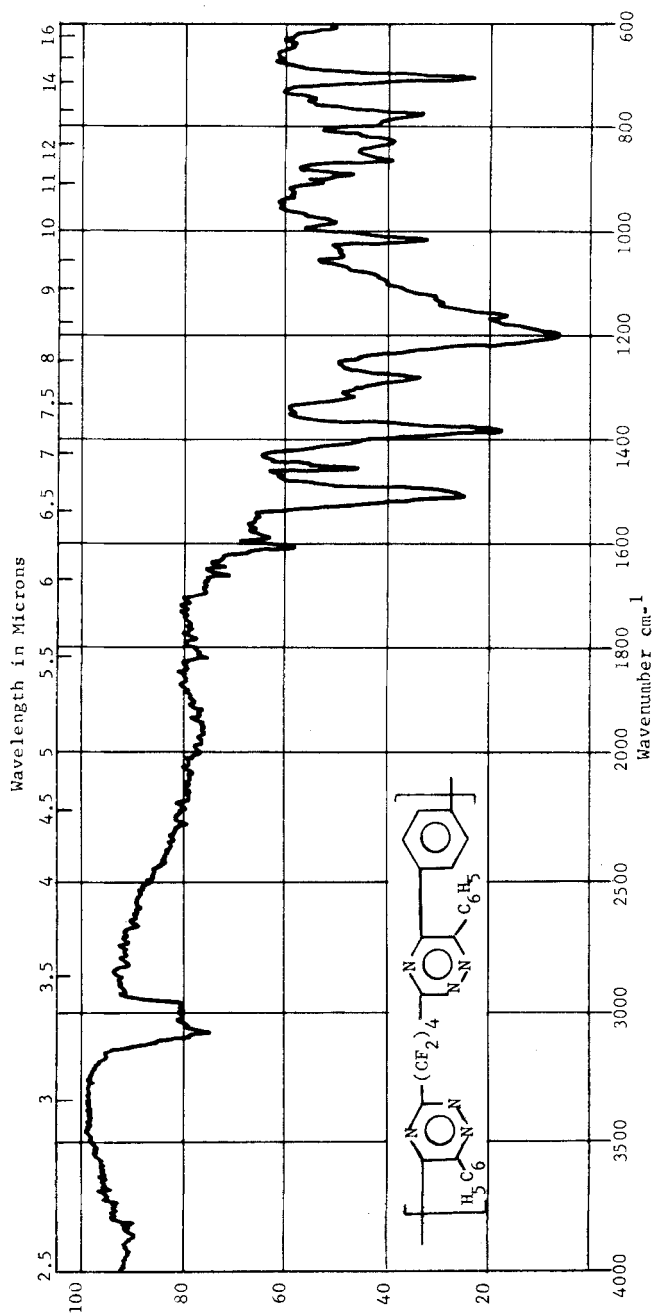
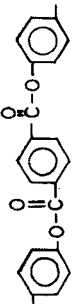
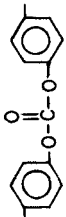


FIG. 4. Infrared spectrum (film) of poly-3,3'-(octafluorotetramethylene-5,5'-p-phenylene-di(5,6-diphenyl-as-triazine).

7	4		140	0.98	178	-	-	380	439 (39)	-	-	
8	4		90 160 400	0.39 0.35 0.28	155	142	310	405	320	413 (20)	-	-

^aInherent viscosity, 0.5% m-cresol solution at 25°C.

^bGlass transition temperature, DSC = differential scanning calorimetry at $\Delta T = 20^\circ\text{C}/\text{min}$, TMA = thermal mechanical analysis at $\Delta T = 5^\circ\text{C}/\text{min}$.

^cThermogravimetric analysis data at $\Delta T = 10^\circ\text{C}/\text{min}$, T_1 = temperature of initial weight loss, T_2 = temperature of initial break, $Y_{800} = \% \text{ char yield at } 800^\circ\text{C}$.

^dOn films.

^eElemental analysis after 160 hours: Calculated for $(\text{C}_{28}\text{H}_{14}\text{N}_6\text{F}_8\text{O})_n$: % C, 57.34; % H, 2.40; % N, 14.33; % F, 25.91. Found: % C, 57.26; % H, 2.43; % N, 14.28; % F, 26.04.

the rate of polymerization of perfluoroadipamidrazone with *p*-bis(phenylglyoxylyl)benzene can be increased with elevated temperatures, but heat should not be applied immediately. If so, high molecular weight polymer is not attained.

Thermal Evaluation

Thermal characterization involved thermogravimetric analysis (TGA) at $\Delta T = 5^\circ\text{C}/\text{min}$, differential scanning calorimetry (DSC) at $\Delta T = 20^\circ\text{C}/\text{min}$, thermomechanical analysis (TMA, film elongation) at $\Delta T = 5^\circ\text{C}/\text{min}$, and isothermal aging of films at 232°C in air. Figure 5 presents representative TGA curves with T_1 , the temperature of initial weight loss, and T_2 , the temperature of the initial weight loss break. The thermal stability, particularly T_2 , of the perfluoroalkylene-containing polymers is higher than that of the nonfluorine-containing all-aromatic analogs ($T_2 = 390$ to 420°C) [2, 7]. The thermal stability of polymer No. 8 (carbonate containing) was significantly lower than the other polymers as anticipated due to the presence of the less-stable carbonate group. The general shape of the TGA curves indicating a two-stage breakdown is characteristic of polyphenyl-as-triazines [2, 7].

The apparent glass transition temperature (T_g) as determined by DSC was taken as the inflection point of the ΔT vs temperature curve as shown in Fig. 6. Powder samples were heated in nitrogen to 250°C , cooled at a ΔT of $1^\circ\text{C}/\text{min}$, and rerun. For most samples the intensity of the T_g transition increased after the annealing cycle. The apparent T_g was also determined on certain films by observing their elongation as a function of temperature (Fig. 7). The temperature where the maximum change in the slope occurred was taken as the T_g . Although the thermal history of each polymer was essentially the same, the molecular weight as indicated by the η_{inh} varied considerably, which makes a valid T_g comparison questionable. The following T_g trend is generally prominent in polymers: *p*-phenylene > *m*-phenylene > *p,p'*-oxydiphenylene. In the series shown in Table 3, the *m*-phenylene polymer (No. 4) exhibited a T_g lower than that of the *p,p*-oxydiphenylene polymer (No. 5), possibly due to its lower molecular weight.

Isothermal weight loss studies on three of the polymer films were conducted at 232°C in circulating air to determine their relative thermooxidative stability. The films were prepared by

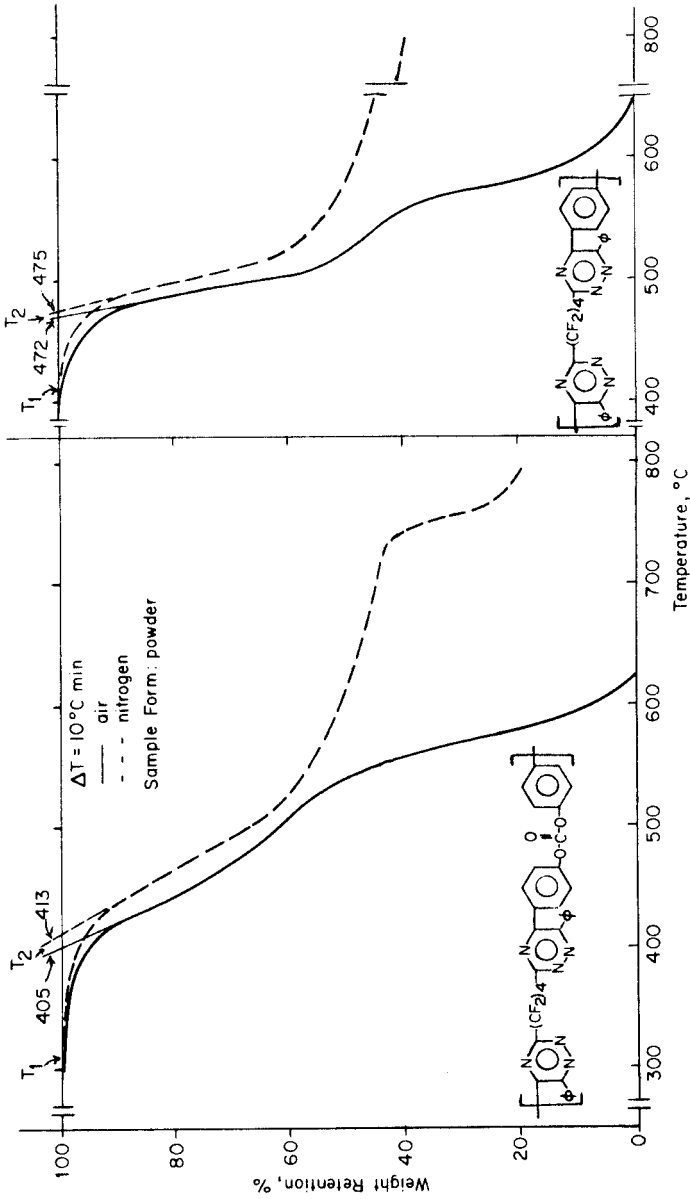


FIG. 5. Thermogravimetric analysis of perfluorotetramethylene phenyl-as-triazine polymers.

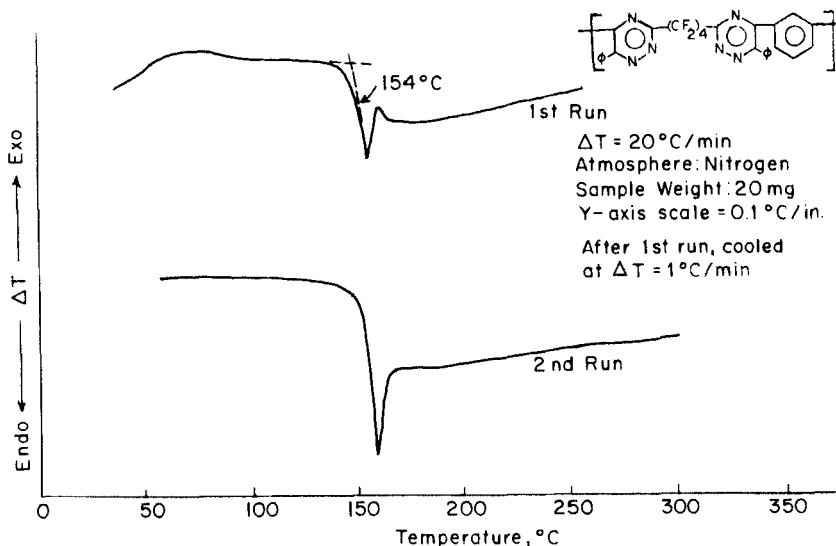


FIG. 6. Differential scanning calorimetry curve of a perfluoro-tetramethylene phenyl-as-triazine polymer.

casting the *m*-cresol (or chloroform) solution onto glass and drying to a final temperature of 140°C in vacuo for 18 hr. As indicated in Table 3, polymers Nos. 3 and 5 exhibited weight losses of only 5.2 and 4.5%, respectively, after aging for 800 hr. Although each of the films curled and darkened slightly during this thermal exposure, the films of polymers Nos. 3 and 5 retained good flexibility (could be fingernail creased but failed when creased again) after 800 hr. The T_g 's of polymers Nos. 3 and 5 increased by 4 and 7°C , respectively, after aging.

Hydrolytic Stability

The hydrolytic stability of several partially fluorinated as-triazine polymers was determined by boiling powder samples in water for 24 hr and observing any change in the η_{inh} and IR spectrum. All of the polymers evaluated showed essentially no change in the η_{inh} and IR spectra, including the carbonate-containing polymer (No. 8). A negligible decrease in the η_{inh} (0.87 to 0.84) of the *m*-phenylene

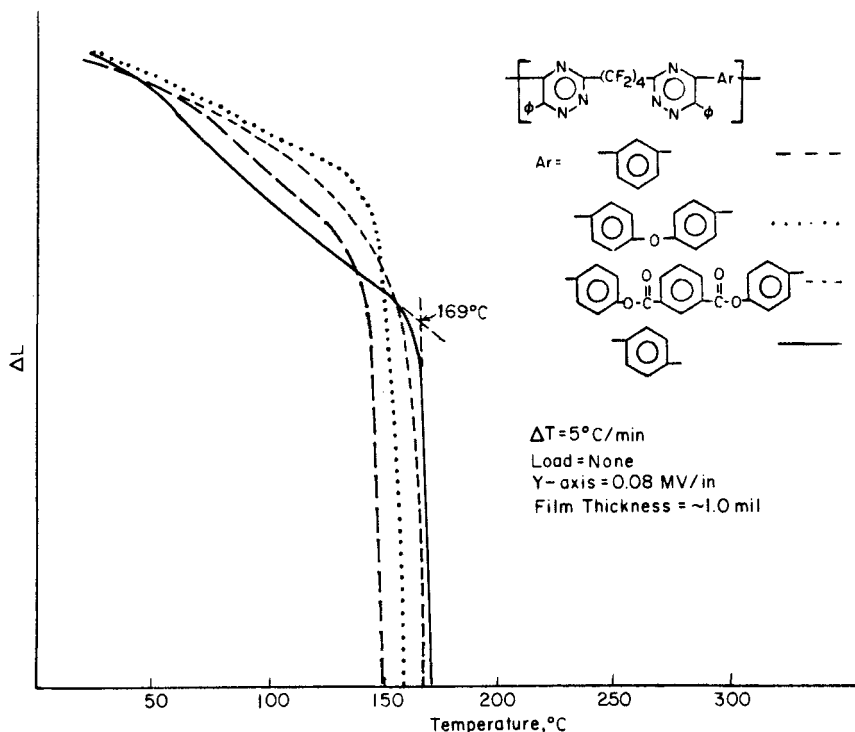


FIG. 7. Elongation behavior of perfluorotetramethylene phenyl-as-triazine polymer films.

ester-containing polymer (No. 6) was observed although no change was apparent in the IR spectrum. Polymers Nos. 4 and 5 in the form of powders were also refluxed in 10% aqueous sodium hydroxide for 8 hr and again displayed only negligible changes in the η_{inh} (e.g., for polymer No. 5, 0.90 to 0.87).

Solubility

The partially fluorinated as-triazine polymers exhibit excellent solubility in a variety of solvents such as acetone, methylene chloride, chloroform, sym-tetrachloroethane, m-cresol, tetrahydrofuran, and highly polar solvents such as N,N'-dimethylformamide and dimethylsulfoxide. Solubility tests were conducted at ambient temperature at a concentration (w/v) of 10%.

EXPERIMENTAL

The experimental procedures for the preparation of the perfluoroalkyleneamidrazones and the bis(1,2-dicarbonyl) monomers are provided in the references cited in Table 1.

4,4'-Bis(benzilyl)carbonate

This monomer was prepared from the interfacial reaction of 4-hydroxybenzil and phosgene. To a mixture of 4-hydroxybenzil (33.9 g, 0.15 mole) in 1 N NaOH (150 ml), 1,2-dichloroethane (50 ml), and tetrapropylammonium bromide (1.0 g) serving as an emulsifying agent, phosgene was bubbled through the churning emulsion at a rapid rate until the reaction mixture was neutral. An additional 5 ml of 1 N NaOH was added and the phosgene addition was resumed until the reaction was again neutral. The organic layer was separated, washed with water, and added to methanol to precipitate a yellow solid (quantitative yield). Recrystallization from benzene afforded yellow crystals, mp 159.0 to 160.0°C, whose IR spectrum was consistent with the proposed structure. The elemental analysis is given in Table 1.

3,3'-Perfluorotetramethylenedi(5,6-diphenyl-as-triazine)

Benzil (2.10 g, 0.01 mole) and perfluoroadipamidrazone (1.57 g, 0.005 mole) were stirred in m-cresol (15 ml) at ambient temperature for 18 hr to yield a white suspension. Filtration followed by washing with methanol provided a white solid (0.94 g), mp 194.5 to 195.5°C (dec). The filtrate was concentrated to dryness in vacuo (90°C) to yield a bright yellow solid (2.2 g), mp 178 to 183°C, which was recrystallized from benzene:ethanol (1:4) to yield bright yellow needles (1.7 g), mp 185 to 186°C. The elemental analysis is given in Table 2.

Polymers

The polymers were prepared on a 0.01 mole scale in m-cresol at a concentration (w/v) of 10%. The bis(1,2-dicarbonyl) monomer and the perfluoroalkyleneamidrazone were weighed into a flask, the appropriate volume of m-cresol added, and the mixture stirred at ambient temperature in air for the time designated in Table 3. Samples were periodically isolated from the clear yellow viscous

solutions by precipitation in methanol, followed by washing in methanol and drying at 80°C in vacuo for 18 hr. Characterization of the polymers is provided in Table 3.

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