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Kinetics of Thermal Degradation of Poly[bis(2,2,2-trifluoroethoxy)phosphazene]

Martel Zeldin,* Won Ho Jo,† and Eli M. Pearce

Polytechnic Institute of New York, Brooklyn, New York 11201. *Received May 14, 1979*

ABSTRACT: Poly[bis(2,2,2-trifluoroethoxy)phosphazene] was depolymerized at 350 °C under vacuum. Volatile products were characterized by infrared, ^{31}P NMR, and gas chromatographic–chemical ionization mass spectral techniques; the predominant product was the cyclic trimer. A random scission–partial unzipping mechanism was supported by fitting molecular weight change–weight loss data to theoretical curves. An average zip length of 35 chain units was found. An activation energy of 43 kcal/mol was observed from isothermal TGA data at different temperatures. A similar value was obtained from dynamic TGA at different heating rates. A reaction order of 0.8 was found and interpreted in terms of *quasi*-first-order kinetics.

Although synthetic techniques for the preparation of polyphosphazenes are well established and numerous studies of their physical and dynamic-mechanical properties have been reported,[1-12] the mechanism of thermal degradation of this class of substance is still unresolved. MacCallum and Tanner[13] have shown that pyrolysis of polyphosphazenes leads to a mixture of ring and low molecular weight chain oligomers. Allcock et al.[14,15] analyzed the decomposition products of polyphosphazenes by gel permeation chromatography (GPC), solution viscosity, and mass spectrometry. Their data on poly[dialkoxyphosphazenes] qualitatively support both a random cleavage and unzipping mechanism. However, a depolymerization process involving chain-end initiation followed by unzipping or other mechanisms could not be precluded.

Recently, Valaitis and Kyker[16] reported a study of the thermal degradation of a polyphosphazene containing a mixture of trifluoroethoxy and (octafluoropentanyl)oxy substituents by isothermal TGA and GPC. The data were interpreted in terms of a random polymer scission process; however, differentiation between this mechanism and one involving continuously random scission and the determination of certain important kinetic parameters (e.g., average zip length, reaction order) by application of theoretical treatments were not accomplished. Furthermore, the presence of oligomers and multiple substituents in the polymer make evaluation of activation parameters difficult to determine and interpret.

In the present study we report the kinetics of thermal decomposition of poly[bis(2,2,2-trifluoroethoxy)phosphazene] by following molecular weight changes with reaction conversion. The experimental data are fitted to equations derived by MacCallum[17] and support a mechanism involving a random chain scission process followed by a partial unzipping of the fragments to give cyclic oligomers. In addition to the calculation of the average zip length, the reaction order, which is implied from curve fitting, has been determined experimentally. Additionally, the activation energy has been obtained from both isothermal and dynamic thermogravimetric analysis.

Theory

Kinetic equations based on MacCallum's theoretical treatment for thermal depolymerization are given below. According to theory, depolymerization mechanisms can be divided into two groups categorized by the nature of the initiation reaction, i.e., random scission along the polymer molecule backbone or initiation at the polymer chain ends. Each category can be further divided into (a) initiation followed by partial unzipping and (b) initiation followed by complete unzipping. Relationship 1 is generally applied

$$W = N(\overline{\mathrm{Dp}})m \qquad (1)$$

for any polymer degradation, where W is the weight of the polymer at time t, N is the number of molecules in the sample at time t, $\overline{\mathrm{Dp}}$ is the number-average degree of polymerization of the sample at time t, and m is the repeat-group molecular weight. Differentiation of (1) with respect to t gives

$$\frac{1}{m}\frac{\mathrm{d}W}{\mathrm{d}t} = N\frac{\mathrm{d}(\overline{\mathrm{Dp}})}{\mathrm{d}t} + \overline{\mathrm{Dp}}\frac{\mathrm{d}N}{\mathrm{d}t} \qquad (2)$$

For random initiation followed by an incomplete unzipping process and assuming that the depolymerization follows first-order kinetics with respect to sample weight

$$\mathrm{d}N/\mathrm{d}t = kW/m \qquad (3)$$

$$-\mathrm{d}W/\mathrm{d}t = kWZ \qquad (4)$$

where Z is defined as the zip length. Combination of (1)–(4) followed by integration gives

$$M = f(1 - C)/(C + f) \qquad (5)$$

where $M = \overline{\mathrm{Dp}}/\overline{\mathrm{Dp}}_0$, $f = Z/\overline{\mathrm{Dp}}_0$, and C is the fractional conversion, $(W_0 - W)/W_0$.

For random initiation followed by complete unzipping, Z is defined as some multiple of $\overline{\mathrm{Dp}}$ (eq 6), where b is a

$$Z = b(\overline{\mathrm{Dp}}) \qquad (6)$$

parameter related to the polydispersity of the polymer. Combining (3), (4), and (6) and integrating (2) gives

$$1 - C = M^{(b/b-1)} \qquad (7)$$

For terminal initiation followed by partial unzipping

$$-\mathrm{d}N/\mathrm{d}t = 0 \qquad (8)$$

From (2), (4), and (8) and integration one gets

$$M = 1 - C \qquad (9)$$

Finally, for terminal initiation followed by complete unzipping

$$-\mathrm{d}N/\mathrm{d}t = kN \qquad (10)$$

Combining (1), (2), (4), and (10) and integrating gives

$$M = 1 \qquad (11)$$

Representative theoretical curves from (5), (7), (9), and (11) are summarized in Figure 1 (insert), which is a plot of the fractional number-average molecular weight as a function of fractional conversion. Line ACG corresponds to degradation by a chain-end initiation followed by a complete unzipping process (eq 11). Since initiation is the rate-determining step, no change in molecular weight with

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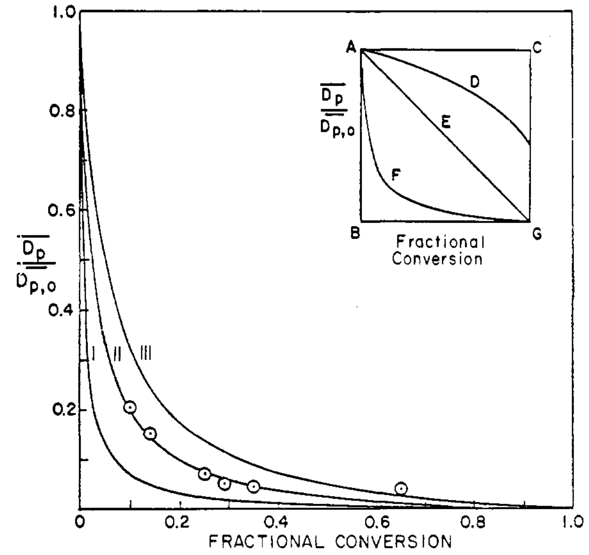

Figure 1. Plot of the fractional molecular weight of degraded polymer as a function of weight loss. Circles represent data points; curves represent theoretical lines for f ($=Z/\overline{Dp}_0$): (I) $f = 0.0080$; (II) $f = 0.0279$; (III) $f = 0.0558$. Insert is for the theoretical plots from eq 5, 7, 9, and 11 (see text).

conversion is expected. If chain-end initiation is followed by incomplete unzipping (eq 9), a molecular weight change which is directly proportional to the reaction conversion (AEG) is obtained. A mechanism involving random scission followed by complete unzipping will result in a slow decrease in molecular weight with reaction conversion (ADG), whereas random initiation followed by incomplete unzipping will result in a rapid decrease in molecular weight with conversion (AFG). In both these cases a family of curves, which depend on the zip length, can be generated. Finally, a random scission process without unzipping is expected to decrease molecular weight strikingly without appreciable weight loss (ABG).

Theoretical treatments for determining kinetic parameters from TGA have been developed.[18-23] For example, Reich[20] derived (12) and (13) to give the reaction order

$$\frac{S_1}{S_2} = \frac{W_{1,c}}{W_{2,c}} \frac{\log (W_{0,c}/W_{1,c})}{\log (W_{0,c}/W_{2,c})} \quad \text{when } n = 1 \qquad (12)$$

$$\frac{S_1}{S_2} = \left(\frac{W_{1,c}}{W_{2,c}}\right)^n \left[\frac{1 - (W_{1,c}/W_{0,c})^{1-n}}{1 - (W_{2,c}/W_{0,c})^{1-n}}\right] \qquad (13)$$

from a single TGA thermogram, where $W_{i,c}$ is the weight fraction of material remaining (W_i) less the weight fraction of inactive material and S_i is defined as $\mathrm{d}W_i/\mathrm{d}(1/T)$.

Finally, Flynn and Wall[21] have shown that the Arrhenius activation energy can be obtained from weight loss–temperature data at different heating rates β (eq 14).

$$E_a = -4.35[\mathrm{d}(\log \beta)/\mathrm{d}(1/T)] \qquad (14)$$

Experimental Section

1. **Preparation of Poly[bis(2,2,2-trifluoroethoxy)phosphazene].** Carefully purified $(PNCl_2)_3$ (16.77 g) was placed in a glass tube, degassed by melt–freezing under vacuum, and sealed. The tube was heated to 250 °C for 44 h. The contents of the tube became an immobile, transparent solid which, on cooling, dissolved in dry THF (100 mL) overnight under N_2. The polymer solution was added dropwise to a solution of sodium 2,2,2-trifluoroethoxide prepared by adding sodium (0.32 mol) to 2,2,2-trifluoroethanol (35 mL) in THF (130 mL). The reaction mixture was heated to reflux under dry nitrogen for 25 h with stirring. After the reaction, the polymer was precipitated with benzene and the solution was neutralized with dilute HCl. The precipitate was filtered, washed with a mixture of water and ethanol, and dried under vacuum. The polymer was purified by precipitation with water from an acetone solution and then with benzene from a THF solution to remove salt and cyclic oligomers, respectively. A total of 14.2 g (40.4% based on $(NPCl_2)_3$) of product, $[NP(OCH_2CF_3)_2]_n$ was obtained. The DSC of the purified polymer indicated no residual ring oligomers.

Table I
Molecular Weight Determination of Degraded Polymers

C	$[\eta]$, dL/g	$\overline{M}_n{}^a$	$\overline{Dp}$	$\overline{Dp}/\overline{Dp}_0$
1	1.14	305 000	1255	1
0.9	0.3370	61 500	253	0.207
0.86	0.2720	46 400	191	0.152
0.75	0.1470	20 600^b	85	0.068
0.71	0.1175	15 400^b	63	0.050
0.65	0.1090	13 900	57	0.045
0.35	0.1015	12 700	52	0.041

[a] Determined by $[\eta] = 7.7 \times 10^{-5}\overline{M}_n{}^{0.76}$. [b] Determined by vapor phase osmometry and used for determination of K and a in the Mark-Houwink equation.

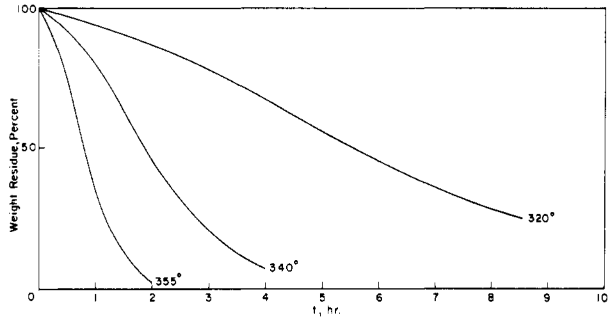

Figure 2. Isothermal TGA thermograms for the degradation of poly[bis(2,2,2-trifluoroethoxy)phosphazene] as a function of time at 320, 340, and 355 °C.

2. **Thermolysis Techniques.** About 300–400 mg of $[NP(OCH_2CF_3)_2]_n$ was decomposed at 350 °C (±2 °C) under vacuum in a tube furnace (Diffusion Engineering Co.) which was calibrated by a chromel–alumel thermocouple. The tube was removed from the furnace after the appropriate time interval. The residue was weighed to obtain weight-loss data. Volatile degradation products were collected and characterized (see later). The molecular weight of the residues below 30 000 (Table I) was determined by osmometry (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.). The molecular weight of the residues above 30 000 was obtained from intrinsic viscosity data and the Mark–Houwink equation (Table I).

3. **Viscosity Measurements.** Solution intrinsic viscosity data in acetone (Table I) were obtained with a Cannon-Ubbelohde dilution viscometer at 25 °C. Kinetic energy corrections were neglected since flow exceeded 110 s. Intrinsic viscosities were determined by extrapolating reduced viscosities to zero concentration.

4. **Thermogravimetric Analysis.** The isothermal TGA thermograms (Figure 2) were obtained at 320, 340, and 355 °C under vacuum by using a Du Pont 950 thermogravimetric analyzer combined with a Du Pont 990 thermal analyzer. Rate data (k, first-order specific rate constant) as a function of percent volatilization is given in Figure 3. Dynamic TGA thermograms (Figure 4) were obtained at four different heating rates (0.0833, 0.167, 0.333, and 0.833 °C/s) under an atmosphere of dry nitrogen at a flow rate of 40 mL/min. The weight fraction of inactive residue was about 0.02.

5. **Analysis of Degraded Products.** Decomposition products, which are volatile at 350 °C under vacuum, were collected and characterized spectroscopically. The infrared spectrum of the condensed solids is identical with that of the initial polymer.[1] The proton-decoupled ^{31}P NMR spectrum at 36.43 MHz (Bruker HFS-90) exhibits four lines (δ (H_3PO_4) 16.5, -2.5, -4.5, -9.0). Four elutions at 68 (A), 103 (B), 153 (C), and 165 °C (D) are observed in the GC–mass spectrum (Finnigan 3300) chromatogram. The principal masses of the chemical ionization mass spectra of A–D

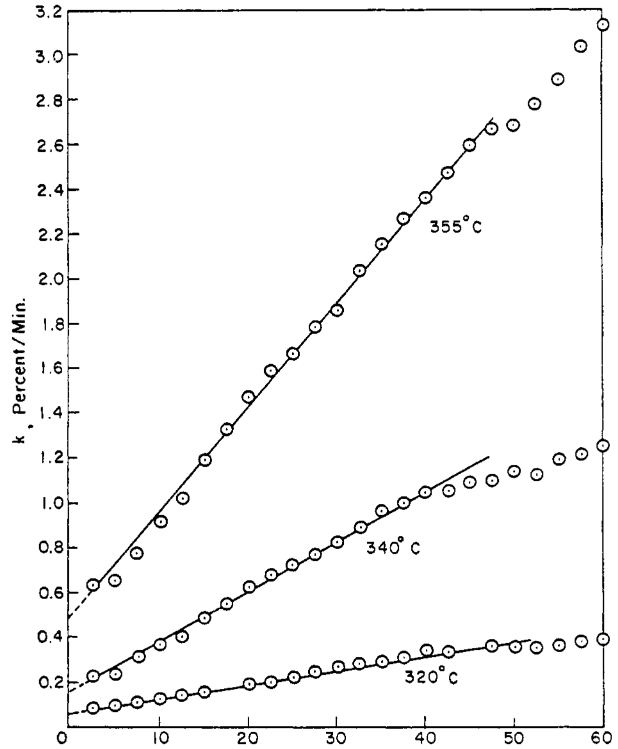

Figure 3. Rates (k) of thermal degradation of poly[bis(2,2,2-trifluoroethoxy)phosphazene] in percent of residue as a function of percent of volatilization at 320, 340, and 355 °C.

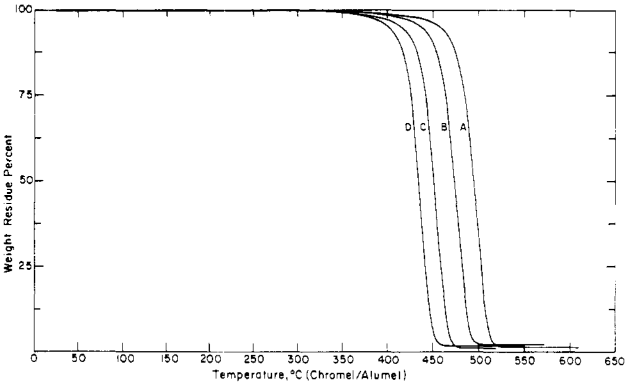

Figure 4. Dynamic TGA thermograms of poly[bis(2,2,2-trifluoroethoxy)phosphazene] at (A) 0.0833, (B) 0.167, (C) 0.333, and (D) 0.833 °C/s.

are summarized in Table II. Unlike earlier studies,[14] chloroethane was not detected.

Results and Discussion

Poly[bis(2,2,2-trifluoroethoxy)phosphazene] was depolymerized under vacuum at 350 °C. The infrared spectrum of the polymeric residues was identical with that of the starting material suggesting, principally, a main-chain rather than a pendant-group scission process.

The nature of the volatile degradation products was determined by ^{31}P NMR spectroscopy and gas chromatography–chemical ionization mass spectrometry (Table II). The proton-decoupled ^{31}P NMR spectrum consists of four lines. Resonances at 16.5 and −9 ppm suggest equivalent phosphorus signals in the cyclic trimer and higher oligomers (e.g., tetramer and pentamer), respectively.[1] These products are verified by GC–MS data which indicate the presence of molecular (M + 1) ions at m/e 730 (B) and m/e 973 (D). There are two additional broad NMR signals of lower intensity which are minor products presumably from thermally induced dehydrofluorination of the cyclic oligomers. Assignments are supported by their mass spectra (m/e(A) 649 for $N_3P_3(OCH_2CF_3)_2(OCH{=}CF_2)_4$ and m/e(C) 892 for $N_4P_4(OCH_2CF_3)_4(OCH{=}CF_2)_4$).

Table II
Principal Masses of the Chemical Ionization Mass Spectra of Polyphosphazene Decomposition Products

	GC %	m/e M + 1	frag-ment[a]	assignment
A	5	650	630	$N_3P_3(OCH_2CF_3)_2(OCH{=}CF_2)_4$
B	88	730	710	$[NP(OCH_2CF_3)_2]_3$
C	2	893	873	$N_4P_4(OCH_2CF_3)_4(OCH{=}CF_2)_4$
D	5	973	953	$[NP(OCH_2CF_3)_2]_4$

[a] Principal fragment ion.

Figure 1 presents the data for the fractional molecular weight change of polymeric residues as a function of conversion (circles) for depolymerization at 350 °C. The number-average molecular weight of two residues was determined by osmometry to evaluate the parameters of the Mark–Houwink equation. The molecular weight of the other residues was then calculated from intrinsic viscosity measurements (Table I) assuming that the polymer samples follow a most probable distribution during thermal degradation.[24] Thus a comparison of the experimental data with the theoretical plots (insert) from MacCallum's equations (eq 5, 7, 9, and 11)[17] supports a depolymerization mechanism involving random initiation followed by incomplete unzipping of the fragments to ring oligomers.

The differentiation between a random scission–unzipping mechanism where the zip length is small (e.g., <10) and a purely random scission process is necessary since similar molecular weight–conversion curves are expected.[25] It has been shown by Simha et al. that the latter mechanism theoretically requires a maximum volatilization rate at 26% weight loss such as occurs in the thermal depolymerization of polymethylene.[25] Since the maximum depolymerization rate for the polyphosphazene used in the present study occurs at about 40% weight loss, a continuously random scission process without unzipping is precluded.

The determination of average zip length requires the fit of experimental data to curves generated from eq 5. Figure 1 contains three sample curves (I, II, and III) for three different f values (0.0080, 0.0279, and 0.0558, respectively; eq 5), where f is the ratio of the zip length to the initial degree of polymerization ($\overline{\mathrm{Dp}}_0$). Since $\overline{\mathrm{Dp}}_0$ is 1255 and the best curve fit occurs with II, one calculates an average zip length of 35 P–N units. Since chromatographic data show that the trimer represents about 90% of the volatile components (Table II), it has been concluded that each random cleavage site generates approximately ten trimer molecules.

The measurement of the rate of weight loss as a function of temperature permits the determination of the Arrhenius activation energy (eq 15).[25] The first-order specific rate

$$E_a = -2.3R[\mathrm{d}(\log k)/\mathrm{d}(1/T)] \qquad (15)$$

constant (k) was obtained from the slope of the isothermal TGA curves (Figure 2) at different fixed conversions. The linear relationship between rate and conversion (Figure 3) to 50% degradation at three different temperatures permits the determination of the temperature coefficient of rate up to 50% weight loss (Table III). Arrhenius plots for 10–45% conversion are reported in Figure 5 and give an average activation energy of 43 kcal/mol. Madorsky has shown that the rate of weight loss by volatilization at different temperatures is applicable to activation energy calculations only when the residue corresponding to the

Table III
k Values at Different Conversions from 320 to 355 °C and Activation Energies for Depolymerization of Poly[bis(2,2,2-trifluoroethoxy)phosphazene]

% conversion	k, %/min 320 °C	340 °C	355 °C	E_a, kcal/mol
0	0.06	0.16	0.50	45
10	0.12	0.38	0.96	44
20	0.19	0.60	1.42	42
35	0.28	0.94	2.12	43
45	0.35	1.16	2.60	42

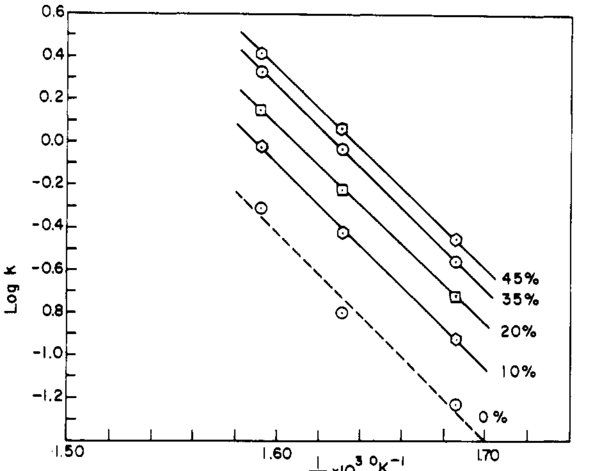

Figure 5. Activation energy plot for thermal degradation of poly[bis(2,2,2-trifluoroethoxy)phosphazene] based on rates at 10, 20, 35, and 45% volatalization and at rates extrapolated to 0% volatilization (broken line).

rate used has the same average molecular weight and the same distribution.[26] This condition is met only at zero conversion when the same material is degraded. k values at zero conversion can be obtained reliably by extrapolation of the lines in Figure 3 and give an activation energy of 45 kcal/mol (Figure 5, dashed lines). Valaitis and Kyker[16] have reported a considerably lower activation energy (20 kcal/mol) for the degradation of mixed trifluoroethoxy and (octafluoropentanyl)oxy polyphosphazenes. It is noteworthy that the low value is more consistent with a chain-end initiation mechanism analogous to that which occurs in the fast-reaction depolymerization of poly(methyl methacrylate) (E_a = 3–6 kcal/mol)[28] and the speculated thermal depolymerization of $(NPCl_2)_x$ (E_a = 22–26 kcal/mol)[29,30] than with a random scission process such as found for the thermal degradation of polystyrene (E_a = 45 kcal/mol) or polyethylene (46–66 kcal/mol).[31] The reason for their low activation energy is probably the presence of low molecular weight oligomers in the polymer which greatly affect initial volatilization rates and, thus, extrapolated values of k. Importantly, calculation of E_a from their rate data above zero conversion gives values close to those reported in this study. Clearly, an activation energy of about 40 kcal/mol is consistent with the energy requirements for cleavage of the P–N bond in polyphosphazenes (i.e., ~70 kcal/mol).[33]

An alternate procedure has been employed to verify the activation energy. Flynn and Wall[21] have shown that activation energies can be determined directly from dynamic thermograms at different heating rates (eq 14). Figure 4 gives the TGA thermograms of the polyphosphazene at 0.0833, 0.167, 0.333, and 0.833 °C/s from which the temperature corresponding to a constant weight loss can be determined. An Arrhenius-like plot (Figure 6) using heating rates as a function of temperature at different fixed-weight residue percent gives an activation energy of 39 kcal/mol which is in excellent agreement with the more acceptable isothermal TGA method. Sebata et al. report a similar value.[32]

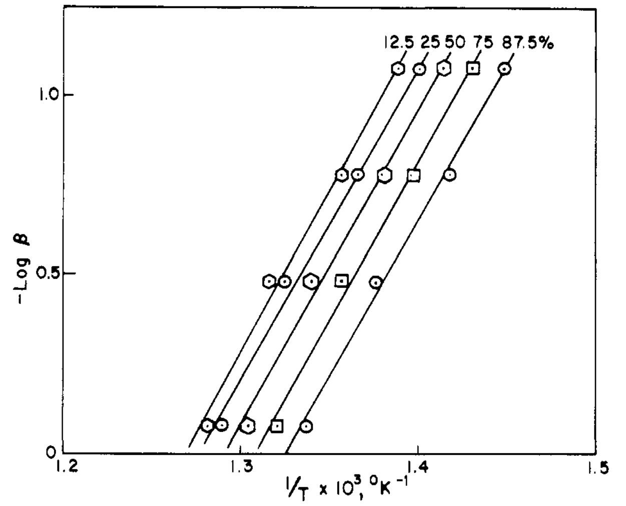

Figure 6. −log β vs. $1/T$ at 12.5, 25, 50, 75, and 87.5% weight loss for the thermal degradation of poly[bis(2,2,2-trifluoroethoxy)phosphazene].

In the absence of a straightforward method for determining reaction order, a master curve method from dynamic TGA data developed by Reich has been used.[20] Specifically, a reaction order calibration curve is generated from eq 12 and 13 for an arbitrarily selected weight residue fraction; $W_{1,c}$ = 0.78, $W_{2,c}$ = 0.18 (the weight fraction of inactive material is 0.02). The experimental value of S_1/S_2 is determined from the measurement of the slope of the weight residue fraction vs. $1/T$ curve at weight residue fractions of 0.8 and 0.1. A value of 0.47 for the 0.167 °C/s thermogram corresponds to a reaction order of 0.8. Other heating rates give identical values.

There are no clear-cut interpretations of reaction order in thermal degradation of polymers.[23,34] Moreover, polymer degradation mechanisms are probably not single-step, simple reactions. It has been assumed in eq 4 and 8 that a random scission initiation process is unimolecular whereas a chain-end initiation is zero order with respect to polymer weight. If cases in which the zip length is larger than the length of the polymer molecule (e.g., PMMA) are excluded, then it is reasonable to regard a reaction order of 0.8 as *quasi*-first order which suggests that poly[bis(2,2,2-trifluoroethoxy)phosphazene] depolymerizes primarily by random scission with a small but finite contribution from chain-end initiation.

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Rotational Relaxation of Chlorobenzene in Poly(methyl methacrylate). 1. Temperature and Concentration Effects

A. C. Ouano*

IBM Research Laboratory, San Jose, California 95193

R. Pecora

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: Rotational motion of chlorobenzene (CB) in poly(methyl methacrylate) (PMMA) over a range of temperature and chlorobenzene concentration is studied by the depolarized dynamic light scattering technique. It was found that the depolarized spectrum of chlorobenzene in PMMA at concentrations of 20 g of chlorobenzene/100 mL or greater shows two widely separated sets of relaxation times, one "fast" on the neat-CB time scale (few picoseconds) and another in the nanosecond and longer time scale (relaxation times typical of macromolecules). The scattered light intensity ratio of the fast to the slow component of the relaxation times was found to increase exponentially with both temperature and concentration. The fast rotational relaxation time was also found to be temperature and CB-concentration dependent.

Introduction

The use of polymers in areas traditionally dominated by steel, glass, and ceramics such as food and electronic-component packaging has continued to grow at an ever-accelerating rate. In this application, the ability of polymeric materials to protect the packaged products from corrosive gases and liquids is of paramount importance. Thus interest in the transport properties of small molecules in amorphous macromolecules has continually intensified in the past 2 or so decades. Scientific studies[1-10] in this area started with the measurement of bulk transport properties, e.g., permeation rates and the diffusivity of gases and liquids in polymers. Although the data obtained by the classical techniques (sorption–desorption measurement) used in the previous studies are very useful, they are also intriguing and often mysterious because they do not follow the relatively simple laws which apply to properties of small-molecule substances. For example, diffusion of gases and liquids in glassy polymers often does not follow Fickian behavior. These complex phenomena arise from the molecular dynamics of the molecules of gases and liquids in polymeric matrices; thus spectroscopic techniques such as NMR[11] and ESR,[12] which are sensitive to molecular dynamics, have been useful in studying them.

A more versatile and perhaps a more powerful technique for studying the motions of molecules in various phases is dynamic light scattering (DLS) photometry. The availability of highly stable lasers has made the rapid development of this technique possible. The book of Berne and Pecora,[13] which offers a comprehensive discussion of the theory and application of this technique, has also contributed in bringing attention to DLS in polymer science.

DLS finds its widest use in the study of the transport properties in liquids. Its application ranges from measurement of center-of-mass diffusion and rotational relaxation of both small molecules and macromolecules in solution[14,15] to the kinetics of polymerization of polystyrene.[16] In this work we used DLS to study the rotational relaxation of chlorobenzene, henceforth referred to as CB, in poly(methyl methacrylate) (PMMA) over a range of temperature and CB concentration.

The CB–PMMA mixture was chosen for this study for the following reasons: (1) CB and methyl methacrylate monomer are miscible in all proportions; (2) CB has a much higher depolarized scattering than PMMA; (3) PMMA and CB are closely matched in refractive index; (4) CB is relatively inert and simply acts as a diluent

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