A was obtained by the sequential polymerization starting from the monofunctional poly(MVE), and B was prepared from the telechelic living poly(CVE). Samples C and D are the corresponding AB diblocks; C has the same MVE/CVE unit ratio as A and B, whereas D is richer in CVE units.

The solutions of samples A and B (0.23 wt %) were cloudy at 15 °C and turned transparent at 21 °C on gradual heating. In contrast, the solutions of the diblock polymers C and D remained cloudy up to 75 °C. ABA triblock copolymers are known to exhibit a better solubility (lower cloud point) in a good solvent for end block than AB diblock copolymers having the same composition.[8] The results shown in Table I are consistent with this fact, demonstrating that the copolymer produced by the $2/I_2$ initiating system is an ABA-type triblock.

In conclusion, this work has shown that telechelic living poly(vinyl ethers) can be prouced by the $2/I_2$ initiating system in nonpolar media and that they could initiate the living polymerization of second vinyl ethers to give ABA triblock copolymers.

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Degradable Polymers. Incorporating a Difunctional Azo Compound into a Polymer Network To Produce Thermally Degradable Polyurethanes

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ABSTRACT: We investigated polymers that feature useful structural or matrix properties at ambient temperature but that convert to soluble materials on heating. To do so we prepared the difunctional azo compound azobis[(3-hydroxypropyl)diisobutylmethane] (BHPA) and characterized its homolytic decomposition kinetics in solution and after incorporation into a cross-linked polyurethane. In poly(propylene glycol) solution, the BHPA first-order homolytic decomposition rate constant, k_d, adhered to the following Arrhenius expression: k_d (s^{-1}) = $10^{(15.4\pm0.43)}$ exp[(−35400 ± 790)/RT]. At 140 °C, the half-life for BHPA thermolysis was 30 min. After chain extension of poly(propylene glycol) with BHPA, trimethylolpropane, and tolylene diisocyanate, BHPA segment thermolysis (as evidenced by N_2 evolution) obeyed the following expression: k_d (s^{-1}) = $10^{(15.0\pm0.091)}$ exp[(−35100 $\bullet$ 170)/RT]. Thus, the BHPA homolysis rate was essentially unaffected by incorporation into the polymer. In the polyurethane network, BHPA decomposition paralleled polymer molecular weight reduction (as evidenced by size exclusion chromatography) and conversion of the polymer from an insoluble to a soluble material. BHPA and related compounds should have general application to preparation of polymers that can be deliberately degraded by heating at a predefined temperature.

Introduction

Considerable polymer research focuses on materials that feature high strength and other useful structural properties under extreme environmental conditions (e.g., elevated temperature and high-intensity irradiation). This research area has an obverse, however, that has received considerably less attention. Polymers are frequently used not only as structural components but also as matrix materials, i.e., as carriers for other chemicals. Examples are polymer matrices for pigments (in paints and coatings), for high-energy compounds (in explosives and propellants), and for drugs (in controlled-release pharmaceuticals). For some applications it is desirable to have a matrix material that retains its physical properties under one set of environmental conditions, but that can be deliberately degraded in a controlled fashion by changing the conditions. Matrix degradation would thereby permit recovery of suspended materials or easy removal (including metabolism and excretion) of the polymer itself.

Several schemes for chemical degradation of polymer matrices (via hydrolysis, oxidation, photolysis, etc.) are possible in principle, but difficult to achieve in practice. As an alternative approach, we have considered thermally labile polymers that degrade simply upon heating. Specifically we have undertaken to prepare and evaluate a difunctional azo compound, azobis[(3-hydroxypropyl)diisobutylmethane] (BHPA), as a monomer suitable for incorporation, e.g., into polyurethanes.

$$HOCH_2CH_2CH_2C(i\text{-}C_4H_9)_2{-}N{=}N{-}C(i\text{-}C_4H_9)_2CH_2CH_2CH_2OH$$

BHPA

As an azoalkane, BHPA should[1] undergo homolytic bond cleavage to yield molecular nitrogen and carbon radicals followed by radical disproportionation to saturated hydrocarbon and olefinic products (vide infra). Inducing these radical reactions in segments of a polymer chain would generate low-molecular-weight fragments and con-

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Table I
Polymer Formulations and Characteristics

desig	component (mmol)[a]		mol wt per cross-link	mol of BHPA per mol of cross-link	mol of N_2 evolved per mol of BHPA[b]	[BHPA], wt %
P-1	BHPA (2) TMP (2) HD (4)	PPG (6) TDI (15)	8300	1	1.06	4.9
P-2	BHPA (3) TMP (2) HD (3)	PPG (6) TDI (15)	8300	1.5	1.14	7.2
P-3	BHPA (4) TMP (2) HD (2)	PPG (6) TDI (15)	8300	2	1.11	9.5
P-4	BHPA (0) TMP (2) HD (6)	PPG (6) TDI (15)	8300	0	c	0
P-5	BHPA (17) TPE (17)	L-35 (50) Hylene W (100)	12500	1	0.95	3.2

[a] Abbreviations used: BHPA (azobis[(3-hydroxypropyl)diisobutylmethane]), TMP (trimethylolpropane), HD (1,6-hexanediol), PPG [2010 molecular weight poly(propylene glycol)], TDI (tolylene 2,6-diisocyanate), TPE 4542 [poly(ethylene oxide) end-capped TMP], L-35 (50/50 ethylene oxide/propylene oxide hydroxy-terminated copolymer), Hylene W [1,1′-methylenebis(4-isocyanatocyclohexane)]. [b] Determined by measuring N_2 evolved from sample of polymer heated 20 h at 140 °C. [c] 2×10^{-2} mol of N_2 evolved per gram of polymer.

comitant changes in polymer physical properties.

We chose BHPA on the basis of literature reports[2-4] that similarly sterically hindered azoalkanes degrade at convenient rates ($t_{1/2} \simeq 1$ h) in the 100–150 °C range. The particular urethane formulations selected for study parallel polymers used as explosive and propellant binders.[5]

However, our objective in investigating BHPA and BHPA-based polyurethanes was not simply to engineer a material for a specific application. Rather we were interested in examining fundamental properties of prototype thermally labile polymer systems using materials that at least model those found in commerce. Specifically we evaluated the following: monomer (BHPA) synthesis, polymer synthesis, monomer and polymer decomposition kinetics, and dependence of polymer properties (molecular weight and tetrahydrofuran (THF) solubility) on time, temperature, and the molar ratio of BHPA to cross-linking agent in the polymer. We find that BHPA thermolysis proceeds as anticipated, both in solution and in polyurethane networks, and that these BHPA-based polyurethanes convert, on heating, to low-molecular-weight, THF-soluble materials.

Results and Discussion

Synthesis. BHPA synthesis was from diisobutyl ketone (1) via reactions 1–4. The literature documents reactions

$$\underset{1}{2R_2C(O)} + N_2H_4 \rightarrow \underset{2}{R_2C{=}N{-}N{=}CR_2} \qquad (1)$$

$$2 + Cl_2 \rightarrow \underset{3}{Cl{-}C(R)_2{-}N{=}N{-}C(R){-}Cl} \qquad (2)$$

$$3 + (CH_2{=}CHCH_2)_3Al_2Br_3 \rightarrow \underset{4}{CH_2{=}CHCH_2C(R)_2{-}N{=}N{-}C(R)_2CH_2CH{=}CH_2} \qquad (3)$$

$$4 + BH_3/H_2O_2 \rightarrow \underset{\text{BHPA}}{HOCH_2CH_2CH_2C(R)_2{-}N{=}N{-}C(R)_2CH_2CH_2CH_2OH} \qquad (4)$$

1 and 2 for preparing the ketazine 2 and the azobis(chloroalkane) 3.[6] The novel Grignard reaction of 3 with triallylaluminum provided the diallyl azo compound 4 in 60% yield. Conventional hydroboration of 4 yielded 59% of the desired product.

Having obtained the difunctional monomer, BHPA, we next prepared several cross-linked urethane copolymers. These differed primarily with respect to the molecular weight per cross-link (XL) and the BHPA:XL molar ratio. Table I summarizes the polymer compositions and characteristics. The Experimental Details section gives further information on polymer preparation. Complete incorporation of BHPA into the polymers was confirmed by determining N_2 evolution from totally degraded samples (Table I). The polymers were swollen, but not dissolved, by CH_2Cl_2, indicating an effectively cross-linked structure.

Decomposition Kinetics. In accordance with accepted mechanisms[1] for azoalkane decomposition, BHPA thermolysis should proceed as in eq 5–7

$$[R'OCH_2CH_2CH_2C(R)_2{-}N]_2 \xrightarrow[\Delta]{} 2R'OCH_2CH_2CH_2C(R)_2\cdot + N_2 \qquad (5)$$

$$2R'OCH_2CH_2CH_2C(R)_2\cdot \rightarrow R'OCH_2CH_2CH_2C(R)_2C(R)_2CH_2CH_2CH_2OR' \qquad (6)$$

$$2R'OCH_2CH_2CH_2C(R)_2\cdot \rightarrow R'OCH_2CH_2CH_2C(R)_2H + (R)_2C{=}CHCH_2CH_2OR' \qquad (7)$$

where R′ is H or a polymer chain.

As indicated in eq 5, BHPA decomposition yields molecular nitrogen and carbon radicals. The latter combine to give alkane (reaction 6) or disproportionate to alkane plus olefin (reaction 7). For the case of R′ = polymer, reactions 5 and 7 produce chain fragmentation and low-molecular-weight products. To test for these reactions, we monitored N_2 evolution vs. time for BHPA in PPG 2010 poly(propylene glycol) solution and for polymer P-3 maintained at 120, 140, and 160 °C. We also monitored physical (THF solubility) and chemical (molecular weight) properties of heated samples of the polymers shown in Table I. The kinetics of BHPA and P-3 decomposition are described below. The subsequent section details the thermal behavior of polymers P-1–P-5.

We calculated first-order decomposition rate constant (k_d) values for BHPA and P-3 according to eq 8

$$\ln (1 - r) = k_d t \qquad (8)$$

where

$$r = (\text{mol of } N_2)_t\text{:initial mol BHPA} \qquad (9)$$

From the temperature dependence of the decomposition kinetics, we calculated Arrhenius parameters according to eq 10. Table II summarizes the kinetic data. BHPA and

$$k_d = A \exp[-E_a/RT] \qquad (10)$$

P-3 decompositions followed first-order kinetics at all temperatures: plots according to eq 8 were linear to at least

Table II
Nitrogen Evolution Kinetics for BHPA and Polyurethane P-3 Decomposition at Elevated Temperature

	BHPA in soln[a]			P-3[b]		
T, °C	100	120	140	100	120	140
k_d ± SD,[c] $s^{-1} \times 10^6$	3.67 ± 0.084	38.3 ± 4.4	386 ± 14	3.08 ± 0.096	33.6 ± 1.6	303 ± 15
$t_{1/2}$,[d] h	53	5.0	0.50	62	5.7	0.63
correln coeff[c]	0.999	0.980	0.997	0.998	0.996	0.994
E_a ± SD,[d,e] kcal/mol		35.4 ± 0.79			35.1 ± 0.17	
log A ± SD[d,e]		15.4 ± 0.43			15.0 ± 0.091	
correln coeff[a]		0.999			0.999	

[a] PPG 2010 poly(propylene glycol) solvent. [b] See Table I. [c] From linear least-squares regression of data according to eq 8. Each rate constant represents data from six time points. [d] Half-time for decomposition, $t_{1/2} = 0.69/k_d$. [e] From linear least-squares regression of data according to eq 10.

Table III
Number-Average Molecular Weight Distribution (M_n) of Polymers P-1–P-3 and P-5[a,b] Degraded at 140 °C[c]

	P-1		P-2		P-3		P-5	
time, min	BHPA decomp per XL	10^{-3} M_n	BHPA decomp per XL	10^{-3} M_n	BHPA decomp per XL	10^{-3} M_n	BHPA decomp per XL	10^{-3} M_n
10			0.25	88	0.35	53		
15	0.28	89	0.43	38[d]	0.57	22[d]	0.29	233
30	0.49	26[d]	0.73	11	0.98	19	0.49	182[d]
45	0.63	13	0.89	12	1.3	10	0.63	60
60	0.74	10	1.1	9.2			0.75	49
90	0.90	11					0.90	50
120	0.93	11			1.9	9.0	0.93	33

[a] See Table I for polymer formulations. [b] Polymer P-4 was omitted because no solutilization was obtained on heating. [c] BHPA decomposed per XL ratio is determined from eq 15 in text. [d] First point tested at which polymer was completely soluble in THF.

75% decomposition in all cases. As seen in Table I, complete P-3 decomposition yielded the stoichiometric amount of N_2. BHPA in PPG 2010 solvent also quantitatively (102 ± 6% average for all three temperatures) liberated N_2, but total gas evolution also included significant (8–28% of initial BHPA) amounts of carbon monoxide. Probably, CO evolution resulted from radical attack (reactions 11–14) on BHPA carbons α to the hydroxyl group:

$$R\cdot + HOCH_2CH_2CH_2 \rightarrow RH + HO\dot{C}HCH_2CH_2 \quad (11)$$

$$R\cdot + HO\dot{C}HCH_2CH \rightarrow RH + HC(O)CH_2CH_2 \quad (12)$$

$$R\cdot + HC(O)CH_2CH_2 \rightarrow RH + \cdot C(O)CH_2CH_2 \quad (13)$$

$$\cdot C(O)CH_2CH_2 \rightarrow CO + \cdot CH_2CH_2 \quad (14)$$

Carbon monoxide evolution was not significant for P-3.

From Table II it is evident that BHPA and P-3 decomposition kinetics were identical at all temperatures.

Arrhenius preexponential and activation energy parameters for BHPA and P-3 are typical for organic azo compounds.[1,7-10] For example, the sterically hindered azoalkane

$$CH_3C(C_6H_5)_2CH_2C(CH_3)_2NNC(CH_3)_2CH_2C(C_6H_5)_2CH_3$$

obeys the following Arrhenius relationship: $k_d = 10^{15.7} \exp[-35000/RT]$.[10] Thus, we conclude that BHPA thermolysis is unaffected when BHPA is incorporated into a polymer backbone.

Polymer Physical and Chemical Properties. We maintained 100-mg samples of each polymer shown in Table I in sealed, evacuated tubes at 140 °C. At timed intervals, the tubes were cooled to room temperature and opened, and 10 mL of THF was added. The molecular weight distribution of each THF-soluble fraction was determined by size exclusion chromatography (SEC). The molecular weight distributions were expressed as number-average molecular weight (M_n) values calibrated vs. polystyrene standards. The absolute polyurethane M_n values determined vs. polystyrene may be in error, but relative M_n values should accurately parallel time-dependent polymer molecular weight changes. At each time point we also calculated the number of polymer chain cleavages per cross-link (XL). This ratio is given by eq 15

$$\frac{\text{mol of BHPA decomposed}}{\text{mol of XL}} = \left[\frac{\text{mol of BHPA}}{\text{mol of XL initial}}\right][1 - \exp(-k_d t)] \quad (15)$$

where $k_d = 303 \times 10^{-6}\ s^{-1}$ (Table II for P-3), t is the decomposition time, and Table I gives the BHPA:XL ratio. Table III summarizes the data for these experiments.

From the table it is clear that the polymers degraded to low-molecular-weight fragments on heating. The molecular-weight decrease was progressive with time, but plateaued at a constant M_n value. The asymptotic approach to a molecular weight minimum is best demonstrated by polymer P-1. The molecular weight minima were essentially identical ((9–11) × 10^3 g/mol) for the three polymers (P-1–P-3) with equal molecular weight:XL ratios (=8300) but the minimum was significantly larger (~30 × 10^3 g/mol) for P-5 with molecular weight:XL = 12500. For polymers P-1–P-3, the molecular weight loss rates paralleled initial BHPA:XL ratios. Thus, at t = 15 min, M_n values were 89 × 10^3, 38 × 10^3, and 22 × 10^3 for P-1–P-3 with initial BHPA:XL ratios, respectively, of 1, 1.5, and 2.

A final point concerns conversion of the polymers from nonsoluble to THF-soluble materials. As shown in Table III, all four polymers with nonzero initial BHPA:XL ratio converted to soluble materials when the ratio of decomposed BHPA to initial XL reached a value of approximately 0.5. Together, the data of Table III reveal several important mechnistic features for the polyurethane degradations. First, the polymers become soluble when the number of chain cleavages equal one-half the number of cross-links. At this point, the polymer changes from a cross-linked three-dimensional structure to a high-molecular-weight linear polymer. Second, as chain cleavages continue, the linear polymer reduces to lower molecular weight fragments reaching a minimum molecular weight. Third, the initial molecular weight:XL ratio controls the molecular weight minimum of degraded polymer whereas the initial degradable monomer:XL ratio determines the overall rate of polymer chain cleavage.

Conclusions

We have demonstrated the feasibility of preparing thermally degradable polymers that incorporate an azo functionality. The demonstration currently rests on a single example, BHPA and BHPA-containing polyurethanes. However, the applicability of the approach is certainly more broad. Our work establishes important fundamentals for designing thermally labile polymers. Specifically we find the following: azoalkane decomposition proceeds with identical rates in solution and when covalently bound to a polymer matrix, azoalkane homolysis produces polymer chain cleavage, the azoalkane:cross-link ratio governs the rate of polymer cleavage, the molecular weight:cross-link ratio equals the minimum molecular weight obtainable, and cross-linked polymer converts to a linear (soluble) material when the ratio of chain cleavages to cross-link equals $^1/_2$.

The above relationships should extend to other azo compounds and polymer types. This extension is significant because azo compound synthesis is straightforward and allows ready substitution of different functional groups. Thus, it should be possible to "tailor" the thermal behavior of a degradable polymer by appropriate selection of azo compound structure. The extensive literature (see ref 1 for a review) on azo compound homolysis kinetics should facilitate the selection of compounds with favorable decomposition kinetics for any required temperature. We have shown that the azodiol BHPA can be incorporated into polyurethanes, but other polymer types can also be considered. Either BHPA or its diallyl precursor, 48 could also form the basis (at least in principle) for polyester, vinyl, or acrylic type macromolecules.

In summary, we consider that the information provided in this report forms the foundation for a new approach to degradable polymer design. Further development of thermally degradable polymers awaits the identification of specific applications and design of specific materials to meet the application requirements.

Experimental Details

The following materials were purchased and used without further purification: methylolisobutyl isobutyl ketone, trimethylolpropane (TMP), 1,6-hexanediol (HD), BASF Wyandott poly(propylene glycol) 2010 g/mol (PPG 2010), tolylene 2,6-diisocyanate (80/20 TDI), BASF Wyandott poly(ethylene oxide) end-capped TMP (TPE 4542), 1:1 ethylene oxide:propylene oxide hydroxy-terminated copolymer (L-35), 1,1′-methylenebis(4-isocyanatocyclohexane) (Hylene W), dibutyltin dilaurate (thermolyte 12). Diisobutyl ketazine (**2**) and azobis(chlorodiisobutylmethane) (**3**) were prepared and purified by the method of Duisman et al.[6] Allylaluminum sesquibromide was via an adaptation of the method of Prevast.[11]

The polymers P-1–P-5 were prepared by using monomers and molar ratios shown in Table I. Preparative methods were identical for all polymers. The synthesis of P-1 is given as an example.

Cross-Linked Polyurethane P-1. A mixture of 2 mmol of BHPA (0.79 g), 6 mmol of PPG 2010 (12 g), 2 mmol of TMP (0.27 g), 3 mmol of HD (0.36 g), and 0.1% dibutyltin dilaurate was heated in bulk under nitrogen at 65 °C for 15 min. The resulting clear mix was cooled to room temperature, and 15 mmol of TDI (2.61 g) was added. After the solution was mixed for 5 min, it was discharged onto a shallow dish, and the uncured polymer was degassed and then cured overnight at 35 °C under nitrogen.

Azobis(allyldiisobutylmethane). Allylaluminum sesquibromide was prepared by refluxing a mixture of 7.83 g (0.29 mol) of aluminum with 52.8 g (0.44 mol) of allyl bromide in 500 mL of diethyl ether with 200 mg of mercuric chloride catalyst for 24 h.

The resulting dark solution was diluted with 100 mL of diethyl ether and then cooled to −10 °C. To this solution was added 19.1 g (0.53 mol) of **3** in 300 mL of diethyl ether dropwise over a 90-min period while the reaction temperature was maintained at −10 °C. After complete addition, the resulting solution was further reacted for 4 h at −10 °C, allowed to warm to room temperature overnight, and then hydrolyzed with 100 mL of saturated aqueous ammonium chloride solution with cooling (~10 °C).

The organic layer was removed, dried over $MgSO_4$, and evaporated to constant weight at room temperature. The resulting oil was purified by passing it through a silica gel column and eluting with hexane. Removal of the solvent yielded 11.8 g (60%) of a bright-yellow mobile oil. NMR and IR analyses were consistent with the assigned structure. Compound purity was ascertained by elemental analysis and by quantitating N_2 evolution from completely degraded samples of neat material.

Azobis[(3-hydroxypropyl)diisobutylmethane] (BHPA). Compound **4**, 11 g (0.03 mol), was dissolved in 60 mL of dry THF, and the solution was cooled to −5 °C. To this solution was added 33 mL of 1 M $BH_3 \cdot THF$ in THF in 0.5-mL portions over a 30-min period while the reaction mixture was maintained at −5 °C. After complete addition, the reaction was maintained at −5 °C for an additional 2 h.

To this solution at 0 °C was added slowly a solution containing 4.4 g of NaOH and 12.1 g of 30% H_2O_2 in 50 mL of water. The resulting mixture was allowed to warm to room temperature and react for an additional 2 h. The solution was then extracted with diethyl ether, and the extract was dried over $MgSO_4$ and evaporated to constant weight at room temperature. This product was eluted from a silica gel column with chloroform and a with 10:90 mixture of methyl alcohol and chloroform. The solvent was evaporated to yield 7.1 g (59%) of a clear oil which on repeated recrystallization from carbon tetrachloride yielded a white solid. NMR and IR spectra were consistent with the required structure. Compound purity was ascertained by elemental analysis and by quantitating N_2 evolution from completely degraded samples of neat material.

Kinetic Measurements. Rates of BHPA decomposition in PPG 2010 solvent and in cross-linked polymer were determined by gas evolution. Samples were accurately weighed into break-seal flasks, degassed by four freeze–pump–thaw cycles, sealed, and heated at 100, 120, or 140 °C for timed intervals. A calibrated gas buret was used to measure the volume of gas evolved from each sample. For the gas analysis, samples were cooled to −196 °C so that only noncondensable gases were measured. Mass-spectral analysis indicated the total gas evolved to be primarily N_2 with varying amounts of CO. The amount of CO present in each sample was quantitated by passing the total gas evolved through a CuO furnace and a −196 °C trap. This procedure converted any CO to CO_2, the latter being condensed at −196 °C. The remaining gas (N_2) was measured on the gas buret; the amount of CO present was determined by subtracting the amount of N_2 from the value for the total gas.

Size Exclusion Chromatography (SEC). Four μ-Styragel columns (pore sizes 10^6, 10^5, 10^4, and 10^3 Å) in series were used for SEC determinations. THF was used as a mobile phase for SEC (flow rate = 1.0 mL/min) and as a solvent for the degraded polymers. A solution of polystyrene standards of known molecular weight (ranging from 800 to 2×10^6 g/mol) was used to calibrate the SEC in terms of molecular weight vs. retention volume.

Registry No. **3**, 94250-14-3; **4**, 94250-15-4; $(CH_2{=}CHCH_2)_3Al_2Br_3$, 67702-85-6; BHPA, 94250-16-5; (BHPA)·(PPG 2010)·(TDI)·(TMP) (copolymer), 94250-17-6.

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Thermal and Oxidative Degradation of Poly(methyl methacrylate): Molecular Weight

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ABSTRACT: The mechanisms of thermal degradation and thermal oxidation of poly(methyl methacrylate) (PMMA) were studied by measuring the molecular weight of rapidly quenched samples thermally degraded in nitrogen and air in the range of temperatures between 200 and 325 °C. Results show that thermal oxidation reduces the degree of polymerization much faster than does thermal degradation. Random scission is the initiation step for both thermal degradation and oxidative degradation. The activation energy for the random scission initiation is 233 kJ/mol for thermal degradation and 64 kJ/mol for oxidative degradation. The average zip length decreases from 2620 to 1340 with an increase in temperature from 258 to 324 °C for thermal degradation. However, the average zip length increases from 20 to 102 with an increase in temperature from 205 to 251 °C for thermal oxidative degradation. A reasonable value of activation energy for the termination reaction in nitrogen, 104 kJ/mol, is obtained only for the assumption of first-order termination.

1. Introduction

In the initiation and growth of a building fire, thermal energy fed back from an external source such as a flame heats and subsequently decomposes interior furnishings which are frequenty made from synthetic polymeric materials. This process of heating the materials and their subsequent decomposition, evolving combustible gases, controls fire initiation and growth. However, this process has often been neglected in theoretical models used to predict ignition, flame spread, and extinguishment because of an apparent lack of understanding of the physicochemical decomposition mechanism. The lack of understanding is more serious for the thermal oxidative decomposition than for the thermal decomposition of polymeric materials. Thermal oxidative decomposition occurs prior to ignition and at the leading edge of a spreading flame.

Poly(methyl methacrylate), PMMA, has been the subject of many studies of ignition[1-3] and flame spread.[4-6] It has been shown that there are two types of initiation reactions of PMMA in vacuum: one is chain-end initiated, due to double-bond terminated polymer chains, and the other is initiated at random positions by a chain scission process.[7-10] After the initiation reaction, depropagation and termination reactions follow. However, most previous studies were based on weight loss measurement to determine a value of the overall activation energy. With the assumption of a first-order termination reaction,[14] or a second-order termination reaction,[11-13] values of activation energy for the termination reaction or for the initiation reaction have been derived by using previously published activation energies for the depropagation reaction.[15,16] There are few studies reported that have directly measured the activation energy of random initiation, the average zip length (the average number of monomer units successively released by depropagation along the length of a polymer chain), and the activation energy of the termination reaction rather than inferring them from overall weight loss measurements.

The thermal oxidative decomposition mechanism of PMMA is not well understood. Kozmina and Shirshova[17] reported that the molecular weight, calculated from the measured intrinsic viscosity, decreases in the presence of oxygen at 200 °C, but not in nitrogen. It was reported[18] that oxygen affected the molecular weight in two ways; one was to accelerate degradation, probably by the formation of peroxides and hydroperoxides and the other was to deactivate free radicals and inhibit degradation. Our recent work[19,20] has shown higher rates of weight loss from thermally irradiated thick PMMA in various oxygen-containing atmospheres than from such samples irradiated in nitrogen. Molecular weights of surface layers obtained from rapidly quenched samples thermally irradiated in oxygen-containing atmospheres are lower than those of samples irradiated in nitrogen. However, there are few data available on the molecular weight, average zip length and activation energies of the various reactions in the thermal oxidation of PMMA.

In this study, molecular weights and weight losses of PMMA, degraded in nitrogen and air under isothermal heating conditions, were measured. The mechanisms of thermal decomposition and thermal oxidation of PMMA were deduced from these results and are reported in this paper.

2. Experimental Section

2.1. Material. The PMMA samples used in this study were commercial Plexiglas G (Rohm and Haas, Inc.); this material is commonly used for studies of ignition and flame spread. [Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply that the material or equipment identified are necessarily the best available for the purpose.] According to the manufacturer, this material contains about 0.1% of a parting agent, 0.5–0.7% of monomer, and a small quantity of ultraviolet absorber. It is made by a free radical polymerization process. One of the polymer chain ends is terminated with a double bond. The measured number average

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