in polymer glasses.[7-11] When secondary relaxations, associated with limited molecular mobility, are considered for PMMA and PS, it is seen that at room temperature the mobility of PMMA should be much greater due to the greater mobility of the acrylate side chain on the PMMA. Even though both polymers have glass transition temperatures at about 100 °C or slightly above, the broad secondary transition[12] for PMMA occurs between about −50 and −30 °C and for PS at about 35–50 °C. This would lead to the expectation that for a poled, unannealed sample, the mobility of the given dye would be greater in PMMA than in PS at room temperature, allowing the dye to rotate more easily in PMMA than in PS. The decrease in the orientation of the dye would cause a more rapid decrease in the SHG intensity in PMMA than in PS.

The dyes used in this study increase in size in the order MNA, DANS, and DR. Using the different dyes will allow the determination of a dynamic distribution of local free volume in these systems. For a given sample at controlled conditions, the decrease in intensity of the SHG signal could be used as a map of dopant mobility versus size, giving a semiquantitative indication of the distribution of free volume in the sample. Preliminary results suggest that disperse red has greater SHG stability than DANS, which, given that DANS is smaller than disperse red, agrees with utilizing this type of approach in examining the local free volume distribution.

Physical aging of these materials should change the polymer physical characteristics in several ways, including a decrease in the specific volume and enthalpy and thus a densification of the material due to a decrease and redistribution of the available free volume.[7,8,11] Since the mobility of the system depends on the degree of primarily through changes in relaxation times.[8] Examining the decreasing SHG signal of polymers doped with these three molecules under different physical aging programs should provide a great deal of information about the free volume in the system and the redistribution of the free volume with thermal treatment. Such results may also lead to better ways to produce doped polymeric materials capable of maintaining desirable SHG properties over a long period of time. Other experiments[13,14] have shown that information about the distribution of free volume in PS and its changes during physical aging can be obtained by using probe molecules.

The degree of orientation of the dopant can be determined by SHG experiments.[5] The amount of dopant orientation will be important in determining both the efficiency of the SHG and the overall obtainable signal and the relaxation of the chains around the dopant molecules. Independent verification of the angle of dopant orientation may be obtained by using a nonlinear Raman spectroscopy or a modified FTIR-ATR dichroism technique, which will be described in a later paper.

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Registry No. PS, 9003-53-6; PMMA, 9011-14-7; DANS, 4584-57-0.

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Thermal Degradation of Saturated Poly(methyl methacrylate)

The thermal degradation of poly(methyl methacrylate) (PMMA) has been studied extensively over the last 40 years. This effort has elucidated many of the primary steps involved in PMMA thermal degradation; however, it has proven difficult to determine accurate Arrhenius parameters for the initiating reaction because of complex kinetics arising from multiple initiation steps combined with depropagation, termination, and chain transfer. We have determined the Arrhenius activation parameters for degradation of saturated PMMA. We believe this is the first accurate determination of these parameters for PMMA.

Early studies (1950s) on PMMA indicated that degradation takes place by chain-end-initiated unzipping.[1-4] It was shown that vinyl-terminated chains degrade at lower temperatures than saturated chains (both formed by the disproportionation termination step). The zip length (number of monomers lost per initiating event) was estimated to be ≈1000.[2]

Later studies suggested that PMMA degradation takes place by a combination of chain-end-initiated depolymerization and random-initiated depolymerization.[5] The rate of mass loss from polymer by a random scission initiated process is described by eq 1 and 2 for zip lengths

$$\text{zip} \gg \text{DP} \qquad \mathrm{d}[\mathrm{M}]/\mathrm{d}t = -k_s\mathrm{DP}[\mathrm{M}] \qquad (1)$$

$$\text{zip} \ll \text{DP} \qquad \mathrm{d}[\mathrm{M}]/\mathrm{d}t = -2k_s(1/\gamma)[\mathrm{M}] \qquad (2)$$

greater than the initial degree of polymerization (DP) or less than DP, respectively,[6] where k_s is the rate constant for chain scission and γ is the reciprocal of the average zip length between initiation and termination. Further restrictions on eq 1 and 2 are that eq 1 assumes a monodisperse molecular weight and eq 2 assumes that termination is either a first-order process or occurs by disproportionation.

Kinetic studies of PMMA degradation have continued to show large variations in the observed Arrhenius parameters (literature values for the activation energy of

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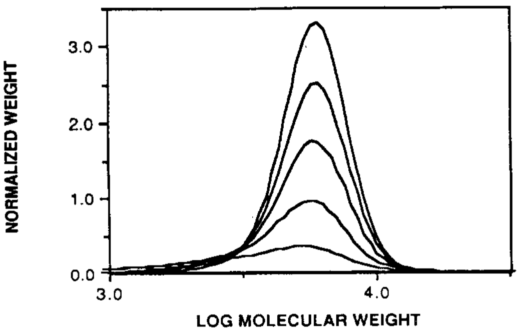


Figure 1. Molecular weight distribution for M_w 6100 PMMA at 0, 20, 40, 60, and 80% degradation.

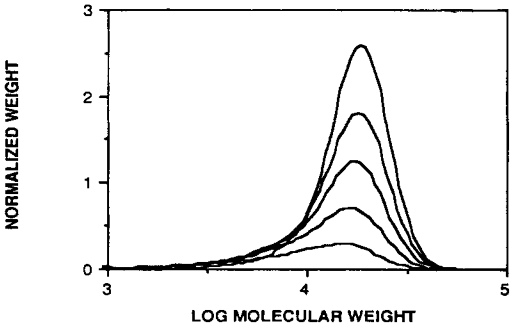
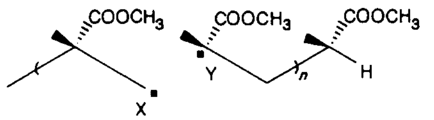


Figure 2. Molecular weight distribution for M_w 19 300 PMMA at 0, 20, 40, 60, and 80% degradation.

PMMA degradation range from 25 to 80 kcal/mol).[7-9] Equation 1 indicates that for monodisperse samples where zip ≫ DP, the rate of mass loss will be a direct measurement of the rate of chain scission. However, for all cases where the zip length is not greater than DP, the rate of mass loss at any given temperature will also be dependent on the rates of unzipping and termination. By studying the degradation of low molecular weight PMMA (so that zip ≫ DP) that is completely saturated and has a narrow polydispersity, we have determined accurate Arrhenius parameters for random chain scission in PMMA.

Results and Discussion. The random scission process that is believed to account for saturated PMMA degradation is shown below. After homolytic cleavage, the polymer chains unzips in both directions. It is certain that the methylene radical (site X) does not undergo depolymerization as readily as the tertiary radical (site Y), and it seems reasonable that if this mechanism actually occurs, both radical ends are tertiary (for example, extrusion of a cyclopropane from the methylene radical end would create a more stable tertiary radical). When the zip length in both directions is much longer than the polymer chain length, the entire molecule will depolymerize after one initiation. Under these conditions the MW distribution will change only slightly (due to the increased rate for higher MW material) and the mass loss will follow eq 1. The activation energy for mass loss will be the activation energy for the initiating random scission. furthermore, the effect of longer chains degrading proportionally faster than shorter chains will change the Arrhenius preexponent not the activation energy.



Figures 1–3 show the effect of thermal degradation on the molecular weight distributions for PMMA with initial DPs of ≈50, 180, and 1000 (M_w = 6100, 19 300, and 125 000, respectively). The molecular weight distribution for the M_w 125 000 polymer changes dramatically during degradation, indicating that this polymer does not meet the requirement of eq 1 that zip ≫ DP. In contrast, the molecular weight distributions for the M_w 6100 and 19 300 polymer are only slightly affected by the degradation process and it is reasonable to apply eq 1 to these polymers. Some low molecular weight material is formed which will affect the data at higher degrees of degradation; therefore our rates were determined from the mass loss between 20 and 40%.

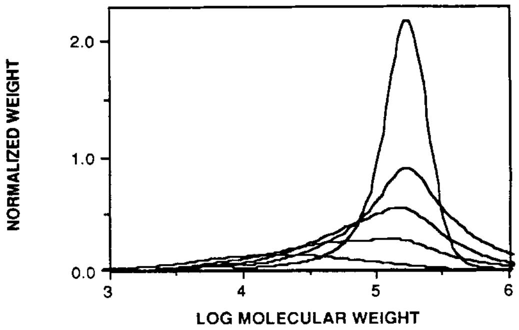


Figure 3. Molecular weight distribution for M_w 125 000 PMMA at 0, 20, 40, 60, and 80% degradation.

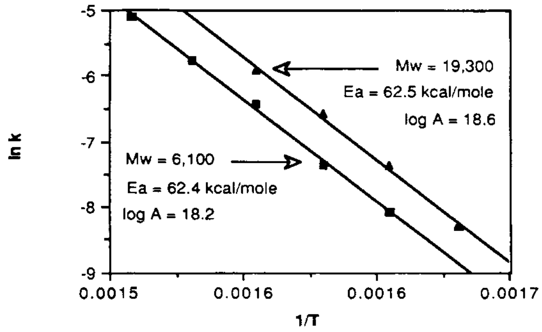


Figure 4. Arrhenius plots for the thermal degradation of M_w 6100 PMMA (squares) and M_w 19 300 PMMA (triangles).

Figure 4 shows Arrhenius plots for PMMA with M_ws of 6100 and 19 300. The observed activation energy for both polymers is (62.4 ± 3.0) kcal/mol and the M_w 19 300 polymer depolymerizes more than twice as fast as the M_w 6100 polymer. These observations are consistent with random initiation followed by complete depolymerization of the polymer chain. The observed preexponential factors must be divided by the number of equivalent sites in a polymer chain to obtain a value that is representative of the actual initiating event. For the two polymers we obtain values of $\approx 2 \times 10^{16\pm2}/\mathrm{s}^{-1}$. A preexponential factor of this magnitude is consistent with rate-determining homolytic cleavage.

In conclusion we have determined the activation energy of the random scission initiation event for thermal degradation of PMMA to be 62 kcal/mol. Furthermore, we have shown that the process occurs with an Arrhenius preexponential factor of $\approx 2 \times 10^{16}\ \mathrm{s}^{-1}$. Future studies are planned to determine accurate activation parameters for degradation of vinyl-terminated PMMA and PMMA chains with incorporated head-to-head linkages.

Experimental Section. Saturated PMMA was prepared by aqueous workup of group-transfer-polymerized PMMA.[10,11] The polymers have narrow molecular weight distributions with $M_w/M_n \leq 1.1$. Molecular weights were determined by GPC using PMMA standards. Isothermal degradation of the polymers was done in a Mettler TG 50 Thermobalance. The quoted error limits are estimates that more than encompass two standard deviations from least-squares analysis of the ln k versus $1/T$ plots. The slopes, intercepts, and standard deviations from the ln k versus $1/T$ plots are slope = 31.21 ± 0.89 kcal, intercept = 42.0 ± 1.4 ln (s^{-1}) for the M_w 6100 polymer and slope = 31.25 ± 1.38 kcal, intercept = 42.7 ± 2.2 ln (s^{-1}) for the M_w 19 300 polymer.

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Registry No. PMMA, 9011-14-7.

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Regio- and Stereospecific 1,4-Polymerization of 2-(Triethylsilyl)-1,3-butadiene

There is considerable interest in stereoregular polymerization of 1,3-diene monomers. Anionic polymerization of isoprene initiated by alkyllithium reagents in hydrocarbon solvents such as cyclohexane yields polyisoprene of narrow molecular weight distribution whose microstructure has been shown by IR,[1,2] ^{1}H NMR,[3] and ^{13}C NMR[4] to be predominantly cis-1,4 (~80%). However, appreciable amounts of trans-1,4 (~15%) and 3,4 (~5%) units are also present. Anionic polymerization of isoprene in the presence of donor solvents such as ether and THF leads to a polymer whose microstructure is predominantly 3,4 (~60%).[2,3] Thus the anionic polymerization of isoprene is regio- and stereoselective but *neither* regio- *nor* stereospecific.

Results and Discussion. We should like to report that regio- and stereospecific anionic polymerization of 2-(triethylsilyl)-1,3-butadiene (I) in hexane solvent at room temperature yields (*E*)-1,4-poly[2-(triethylsilyl)-1,3-butadiene]. Neither (*Z*)-1,4-poly[2-(triethylsilyl)-1,3-butadiene] nor 1,2 nor 3,4 units are found. The reaction is stereospecific. The results are summarized in Table I. As can be seen, GPC analysis reveals a monomodal molecular weight distribution of low polydispersity ($\bar{M}_w/\bar{M}_n$ = 1.3–1.6). The molecular weight of the polymer depends on the ratio of the monomer to initiator. These results are consistent with relatively rapid initiation and the absence of chain transfer and termination reactions during the course of polymerization of I. The microstructure of this polymer is of considerable interest since physical properties of polydienes depend upon the structure of the repeating units. We have determined the mode of the polymerization (1,4; 1,2; or 3,4) and the geometry of the monomer units by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The ^{1}H NMR of this polymer can be seen in Figure 1. Note that in the olefinic region only a single peak at 5.70 ppm (1 H) is observed. For comparison the vinyl CH of (*E*)-3-(trimethylsilyl)-3-octene comes at 5.60 ppm.[6] This strongly suggests that the polymer has an (*E*)-1,4 microstructure. The stereoregularity of the carbon–carbon double bonds in the polymer chain is supported by the ^{13}C NMR in which only two nonequivalent vinyl carbons as well as two distinct allylic carbons are observed. No peaks which could be assigned to either 1,2 or 3,4 structures were observed in either the ^{1}H or ^{13}C NMR spectra. Further, only a single silicon resonance is seen in the ^{29}Si NMR spectrum (see Experimental Section for details). Finally, protodesilation of the polymer by treatment with HI in a mixture of water and methylene chloride yields (*Z*)-1,4-polybutadiene whose structure was determined by infrared spectroscopy.[7] Protodesilation of vinyl silanes has previously been shown to occur stereospecifically with retention of configuration.[8,9] All of these pieces of data are consistent with (*E*)-1,4-poly[2-(triethylsilyl)-1,3-butadiene]; see eq 1.

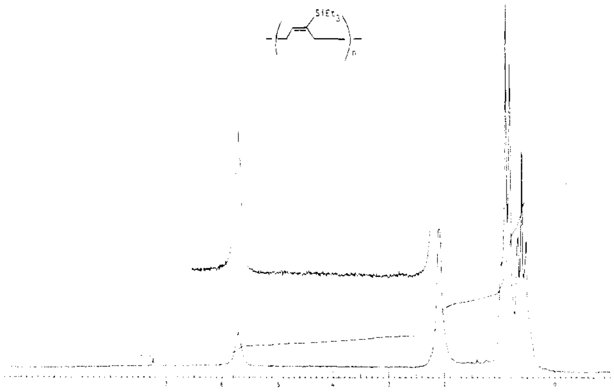
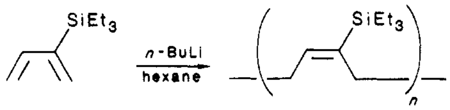


Figure 1. ^{1}H NMR of 1,4-(*E*)-poly[2-(triethylsilyl)-1,3-butadiene].

Table I
Anionic Polymerization of I in Hexane at 25 °C

% *n*-BuLi initiator	time	% yield	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	$\bar{M}_w/\bar{M}_n$
0.5	60 h	62	108.8	67.3	1.61
1.5	30 h	93	18.3	14.0	1.28



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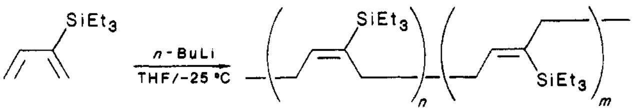

(2)

On the other hand, while anionic polymerization of I in the presence of donor solvents such as THF gave a polymer of 1,4 microstructure, the stereochemistry about the carbon–carbon double bonds was a mixture of *E* and *Z* in which the *E* configuration predominates; see Table II. The ratio of *E* to *Z* was determined by integration of the ^{1}H NMR signals of the vinyl CH protons which are well separated. Thus the *Z* vinyl CH comes at 5.99 ppm while the *E* vinyl CH comes at 5.71 ppm. The ^{1}H NMR of this