tribromoheptane, 119207-04-4; isotactic 2,4,6-trifluoroheptane, 119393-43-0; syndiotactic 2,4,6-trifluoroheptane, 119477-50-8; heterotactic 2,4,6-trifluoroheptane, 119477-51-9.

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(7) It will be noted that, since the total energy of the LDTT conformer is less than that of LDG′G′, the corresponding Kerr constants are at odds with the experimental findings for PVB dimers and trimers (ref 9c). This is no doubt because, in the interest of comparison, we have used the same parameters as Boyd and Kesner,[3a] who in parametrizing their method explicitly sacrificed reproduction of the Kerr effect (see ref 3a, p 3182).
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Thermal Degradation of Poly(methyl methacrylate). 2. Vinyl-Terminated Polymer

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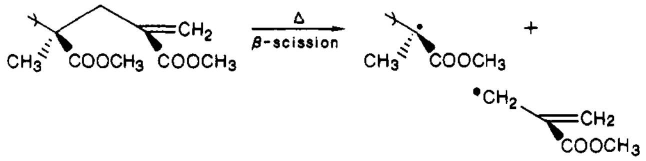
ABSTRACT: It is demonstrated that the thermal degradation kinetics for vinyl-terminated poly(methyl methacrylate) (PMMA-CH=CH$_2$) are dependent on the sample thickness. A systematic study of film thickness on PMMA-CH=CH$_2$ degradation indicates the accepted mechanism of homolytic scission β to the vinyl group is incorrect. A chain-transfer process is proposed that explains the observed results. The source of radicals that initiate degradation is not determined.

Introduction

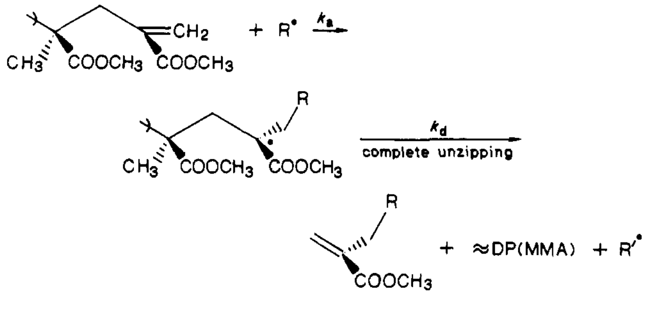
It has been observed that vinyl-terminated poly(methyl methacrylate) thermally degrades at a lower temperature than saturated PMMA (PMMA-H). For example, when free radically polymerized PMMA is heated at 10 °C/min, the unsaturated portion (PMMA-CH=CH$_2$) degrades between 230 and 300 °C, whereas the saturated portion (PMMA-H) degrades between 300 and 400 °C.[1-3] It is generally believed that PMMA-CH=CH$_2$ is less stable due to facile β-scission of the relatively weak C–C bond β to the vinyl group (Scheme I). With short polymer chains the result of Scheme I is end initiation followed by complete unzipping. Accordingly, the rate of degradation will be independent of molecular weight.[4] Studies with model PMMA-CH=CH$_2$ oligomers confirm the low degradation temperature and, in agreement with Scheme I, suggest degradation is independent of molecular weight.[5] The Arrhenius activation energy reported for PMMA-CH=CH$_2$ degradation (~114 kJ/mol) appears low if β-scission is rate limiting.[6]

We are studying the thermal degradation of PMMA-CH=CH$_2$ and report that the major degradation mechanism is not as shown in Scheme I but involves efficient radical transfer to the vinyl chain end (Scheme II). Any reaction that generates a radical R$^\bullet$ (including β-scission if it does occur) will degrade a large number of polymer chains by the chain-transfer process. We believe the radical that transfers the active site to the next chain (R′$^\bullet$) will usually be the species present at the initiation end of the PMMA-CH=CH$_2$ chain. With our samples this will be short oligomeric ($^\bullet$C(CH$_3$)(COOCH$_3$)–R), saturated end group ($^\bullet$C(CH$_3$)$_2$COOCH$_3$), or AIBN radicals ($^\bullet$C(CH$_3$)$_2$CN).

Scheme I



Scheme II



Results and Discussion

Samples of vinyl-terminated PMMA were prepared by using a cobalt chain-transfer catalyst[7] (CoCTC) similar to

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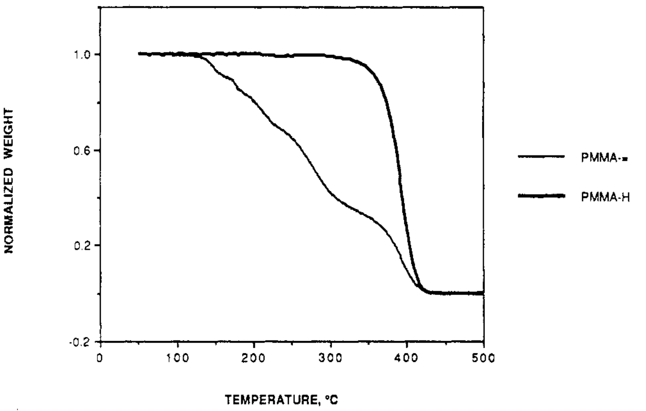

Figure 1. Comparison of TGAs of PMMA-$CH{=}CH_2$ (vinyl-terminated polymer) and PMMA-H (saturated polymer); heating rate = 20 °C/min.

that described previously.[5,8] Methyl methacrylate polymerization using CoCTC is fairly well understood.[8] The polymers used in these experiments were initiated with AIBN. Reaction 1–3 describe the polymerization.

$$(CH_3)_2CNC^\bullet + MMA \rightarrow {}^\bullet C(CH_3)(COOCH_3){-}C(CH_3)_2CN \quad (1)$$

$$^\bullet C(CH_3)(COOCH_3){-}P + CoCTC^\bullet \rightarrow CH_2{=}C(COOCH_3){-}P + CoCTC{-}H \quad (2)$$

$$CoCTC{-}H + MMA \rightarrow {}^\bullet C(CH_3)(COOCH_3){-}H + CoCTC^\bullet \quad (3)$$

Besides reaction 2 (which accounts for most of the termination) polymerization is terminated by the usual processes of coupling and disproportionation. Because reaction 2 accounts for most of the termination, these polymers should have less head-to-head couplings than PMMA polymerized without CoCTC. A complete accounting of all probable end-groups is given here (where P = polymer).

Initiation end

$$CN(CH_3)_2C{-}CH_2{-}C(CH_3)(COOCH_3){-}P$$

$$CH_3{-}C(CH_3)(COOCH_3){-}CH_2{-}C(CH_3)(COOCH_3){-}P$$

Termination end

$$CH_2{=}C(COOCH_3){-}CH_2{-}C(CH_3)(COOCH_3){-}P$$

$$HC(CH_3)(COOCH_3){-}CH_2{-}C(CH_3)(COOCH_3){-}P$$

Regardless of which group is present at the initiation end of the molecule, all molecules terminated with a vinyl group are labeled PMMA-$CH{=}CH_2$ and molecules terminated with a saturated carbon are labeled PMMA-H. The most likely candidates for $R'^\bullet$ in Scheme II are of course $(CH_3)_2CNC^\bullet$ and $(CH_3)_2(COOCH_3)C^\bullet$.

Figure 1 compares a TGA of PMMA-$CH{=}CH_2$ with PMMA-H. As expected, PMMA-$CH{=}CH_2$ degrades at a considerably lower temperature than PMMA-H.

Figure 2 shows molecular weight distributions for PMMA-$CH{=}CH_2$ after 0, 20, 40, 60, and 80% isothermal degradation at 260 °C. The stability of the molecular weight (MW) distribution is remarkable! All molecular weights apparently degrade at the same rate. This observation is consistent with the accepted mechanism (Scheme I); however, we were surprised that such perfect retention of the MW distribution would occur on the basis of Scheme I. We anticipated that some chains would not completely unzip, leading to a noticeable increase in low MW material.

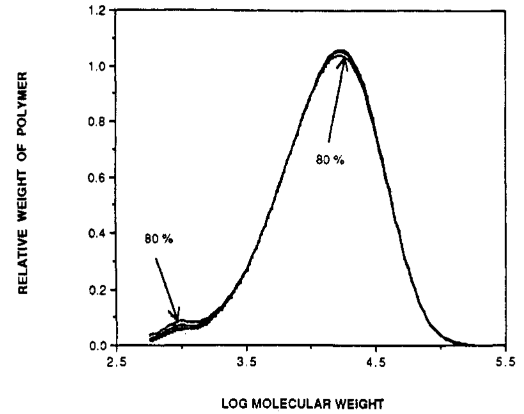

Figure 2. Molecular weight distributions for PMMA-$CH{=}CH_2$ after 0, 20, 40, 60, and 80% isothermal degradation at 260 °C.

Furthermore we noted that samples of differing initial MW degrade at different rates; the observed isothermal rate of degradation increases as MW decreases. This is opposite of that observed with PMMA-H[9] and would appear to be in conflict with the MW distribution data and Scheme I.

We concluded that all of our observations were consistent with a very long zip length (many chains degrading per initiation event) dependent on a combination of the efficiency of chain transfer by mobile free radicals to the vinyl end group and the rate that "live chains" unzip. Consideration of the mechanism outlined in Scheme II led us to conclude that such a chain-transfer process is unavoidable with vinyl-terminated material.

In Scheme II, an active free radical site is formed on the polymer chain end by radical attack at the vinyl terminus of PMMA-$CH{=}CH_2$. Scheme II is not specific about the nature of $R^\bullet$. Indeed an unzipping polymer chain ($PMMA^\bullet$) can react with PMMA-$CH{=}CH_2$; however, we anticipate the rate of reaction between smaller free radical species and PMMA-$CH{=}CH_2$ will be much greater. Scheme II indicates that once the chain process starts, degradation of PMMA-$CH{=}CH_2$ will continue until $R^\bullet$ (or $R'^\bullet$) is removed from the system. Equations 4–6 define the

$$2R^\bullet \xrightarrow{k_t} R{-}R \text{ or } R + R \quad (4)$$

$$R^\bullet + O_2 \xrightarrow{k_{O_2}} RO_2^\bullet \quad (5)$$

$$R^\bullet \xrightarrow{k_D} R_g^\bullet \quad (6)$$

most important reactions responsible for removal of $R^\bullet$ ($R'^\bullet$) from the sample, where k_t is the rate of bimolecular termination, k_{O_2} is the rate of termination by oxygen, and k_D is the rate of $R^\bullet$ diffusion out of the sample.[10,11] Reaction of $R^\bullet$ with PMMA-$CH{=}CH_2$ is not included here because it does not permanently remove $R^\bullet$ from the system; however, the rate of depolymerization of $PMMA^\bullet$ will affect the number of chains that depolymerize before termination.

The importance of $R^\bullet$ loss by evaporation during polymer degradation has been addressed.[12] It is anticipated that the residence time of small, volatile radicals ($R^\bullet$) in the sample can be systematically controlled by varying the sample thickness. The time scale for diffusion out of the system will be proportional to the sample thickness, l (eq 7).[12,13] At 300 °C, the time scale for diffusion of $R^\bullet$ out

$$\tau_D = l^2/(3D_{R^\bullet}) \quad (7)$$

of polymer films of 64, 4, 2, 1, 0.4, and 0.1 μm will be ~3000, 1200, 300, 75, 12, and <1 μs, respectively (using

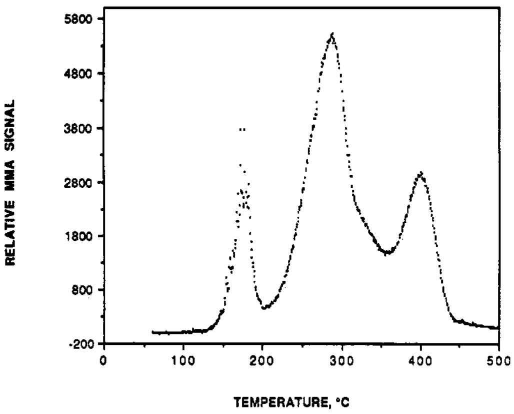

Figure 3. Appearance of MMA when a 60-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

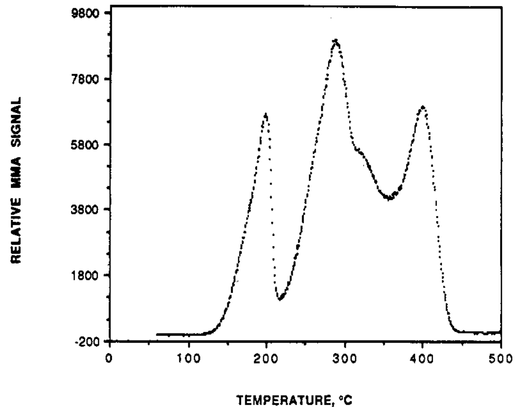

Figure 4. Appearance of MMA when a 4-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

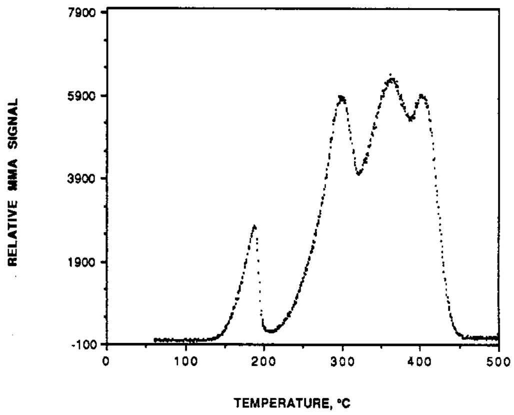

Figure 5. Appearance of MMA when a 2-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

diffusion data for toluene in PMMA above T_g, $\log_{10}D = 5.9 - 5870/T$).[14]

The rate of R$^\bullet$ addition to PMMA-CH=CH$_2$ will be very fast. Using eq 8, we estimate that ~60 μs is the average

$$\tau_{R^\bullet} = 1/(k_a[\text{PMMA-CH=CH}_2]) \qquad (8)$$

time for R$^\bullet$ to react with PMMA-CH=CH$_2$ at 300 °C (using Arrhenius parameters for the reaction of *tert*-butyl radical with MMA; E_a = 25.2 kJ/mol, A = 4.0 × 10^7 s^{-1}, M_n = 14 700, and assuming *tert*-butyl radical is a reasonable model for (CH$_3$)$_2$CNC$^\bullet$ and (CH$_3$)$_2$(COOCH$_3$)C$^\bullet$).[15]

Scheme II indicates the efficiency of PMMA-CH=CH$_2$ degradation will decrease when the residence time for radicals is reduced below the time required for chain transfer to PMMA-CH=CH$_2$. Comparison of the time scale of chain transfer (~60 μs) with the time scale for

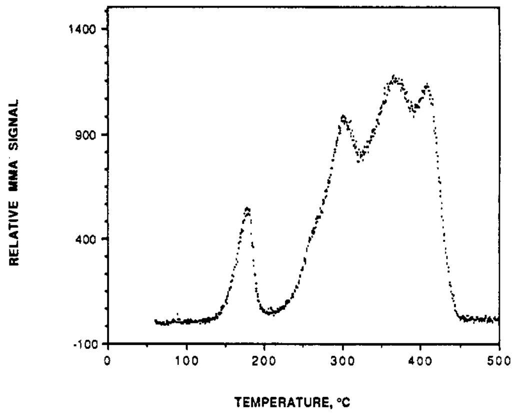

Figure 6. Appearance of MMA when a 1-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

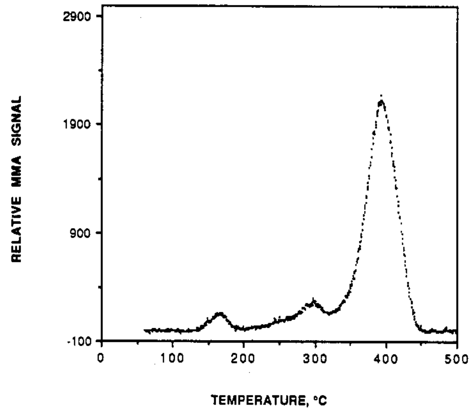

Figure 7. Appearance of MMA when a 0.4-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

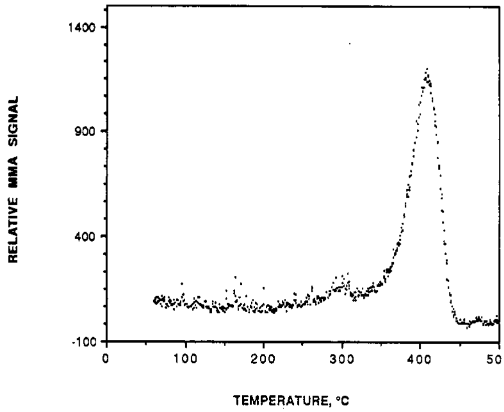

Figure 8. Appearance of MMA when a 0.1-μm-thick film of PMMA-CH=CH$_2$ is heated at 20 °C/min.

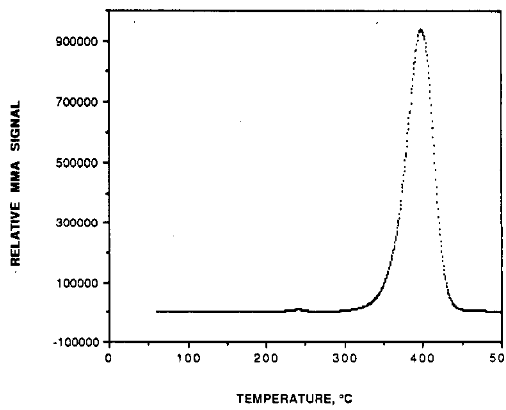

Figure 9. Appearance of MMA when a 60-μm-thick film of PMMA-H is heated at 20 °C/min.

diffusion of R$^\bullet$ out of the polymer film suggests a transition in the mode of degradation will occur when the film thickness is reduced below 1 μm.

Figures 3–8 show the appearance of MMA when PMMA-CH=CH$_2$ (M_n = 14700, M_w/M_n = 1.23) samples of 60, 4, 2, 1, 0.4, and 0.1 μm are heated at 20 °C/min. For comparison, Figure 9 shows the appearance of MMA when a 60-μm film of PMMA-H (M_n = 17000, M_w/M_n = 1.13) is heated at 20 °C/min. With films >1 μm thick, degradation of PMMA-CH=CH$_2$ takes place in predominantly three stages with peaks at ~200, 300, and 400 °C.

The low-temperature peak (150–230 °C) is usually attributed to degradation of polymer with head-to-head bonds (H-H) in the main chain.[2] Because of the chain-termination mechanism for polymerizations using cobalt chain-transfer catalysts, this polymer should have less head-to-head bonds than "typical" free radical polymerized PMMA. Degradation of PMMA-CH=CH$_2$ via Scheme II is the most simple explanation for monomer formation between 150 and 230 °C. One source of radicals at these low temperatures is trace amounts of peroxide from exposure of the sample to tetrahydrofuran (THF). We have noted that the size of this low-temperature peak can vary depending on how the PMMA sample is isolated. The peak is inevitably larger for samples isolated by rotary evaporation of THF (which will leave trace amounts of THF peroxide) than when the polymer is precipitated out of THF with water (in which case THF peroxide will remain in solution). The sample used to prepare films for the data in Figure 8 was isolated by rotary evaporation of the THF. Samples isolated by precipitation give a much smaller low-temperature peak with a correspondingly larger intermediate peak. Regardless of the radical source, a striking observation is that this peak decreases significantly with very thin films, Figures 3–6 vs Figures 7 and 8. It is certain that the fraction of polymer chains containing H-H linkages will not vary with sample thickness.

The intermediate temperature peak is usually attributed to degradation of PMMA-CH=CH$_2$ via Scheme I. The results described hereinabove indicate that PMMA-CH=CH$_2$ degradation below ~300 °C is almost entirely due to reaction via Scheme II. The mechanism outlined in Scheme II allows R$^\bullet$ to degrade many PMMA-CH=CH$_2$ chains. The source of R$^\bullet$ is not certain; however, possible candidates are (1) impurities, (2) small amounts of H-H bonds, (3) β-scission via Scheme I, or (4) random scission. Again, the important feature is that the peak decreases for very thin films, Figures 3–6 vs Figures 7 and 8.

With thin films (~<0.4 μm, Figures 7 and 8) the degradation of PMMA-CH=CH$_2$ is similar to PMMA-H (Figure 9); most of the degradation takes place above 340 °C. In this case the residence time of R$^\bullet$ in the film is too short to allow efficient radical transfer, supporting the mechanism outlined in Scheme II. The degradation of PMMA above 300 °C is known to be initiated by a random scission along the chain followed by complete loss of the chain (when DP < 200).[9] As the efficiency of the chain-transfer process decreases, the only mechanism left for degradation is the random scission process.

As a final confirmation of Scheme II we looked at the degradation of a thin film (~0.4 μm) sandwiched between two quartz plates. We anticipated that the presence of a quartz barrier to diffusion of R$^\bullet$ out of the system will make the thin-film system degrade similar to a thick film. The data in Figure 10 confirm the anticipated result.

Conclusion

The thermal degradation kinetics for vinyl-terminated PMMA (PMMA-CH=CH$_2$) are dependent on the sample thickness. A systematic study of film thickness on PMMA-CH=CH$_2$ degradation indicates the accepted mechanism of homolytic scission β to the vinyl group is incorrect (Scheme I). A chain-transfer process, Scheme II, is proposed that explains the observed results. The source of radicals, R$^\bullet$, that initiate degradation has not yet been determined.

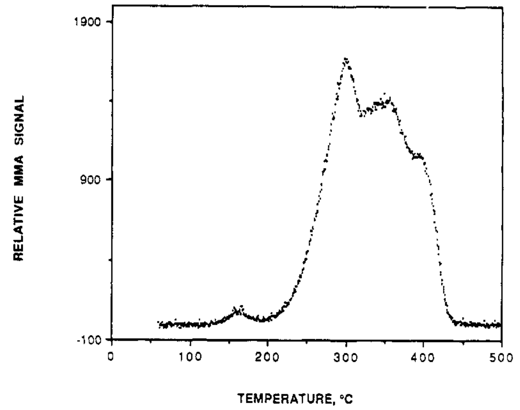

Figure 10. Appearance of MMA when a 0.4-μm-thick film of PMMA-CH=CH$_2$ sandwiched between two 1-mm-thick quartz plates is heated at 20 °C/min.

Experimental Section

PMMA-CH=CH$_2$ was prepared using a cobalt chain transfer catalyst.[7] The PMMA-CH=CH$_2$ samples were dissolved in THF and reprecipitated by addition of excess water. Residual cobalt chain-transfer agent and AIBN initiator were removed (from the samples used in the thin-film studies) chromatographically on a Zorbax ODS reverse-phase column by elution of the polymer sample with a solvent gradient of H_2O/THF/CH_3CN 0.2/1.5/1.5 → H_2O/THF 1/9 over 5 min. The chromatography also fractionated the PMMA-CH=CH$_2$ sample by molecular weight. Samples were isolated by rotary evaporation of the solvent.

The PMMA-CH=CH$_2$ samples used to determine the effect of degradation on molecular weight distribution contained 95% vinyl end groups (estimated on the basis of the percent of the material that degrades below 340 °C) with a M_n = 7800 and M_w/M_n of 2.1. Isothermal degradations were carried out at 260 °C in a Mettler TG 50 thermobalance. The time required for 20, 40, 60, and 80% degradation at 260 °C was 7.2, 13.2, 21.0, and 32.7 min, respectively.

The PMMA-CH=CH$_2$ samples used in the TGA/mass spectrometry studies contained 75% vinyl end groups with a M_n of 14700 and M_w/M_n of 1.23. Thin PMMA films on quartz plates were made as follows. A PMMA solution was prepared by dissolving 10 mg of polymer in 100 μL of methylene chloride and adding 500 μL of *tert*-butyl alcohol. A quartz plate (0.8-cm diameter) was thoroughly cleaned and placed on an optically flat table that floated on a bath of mercury. A film was prepared by spreading 5 μL of the polymer solution on the 0.8-cm quartz plate and allowing the solvent to evaporate. This procedure covered most of the quartz plate with a uniform 0.4-μm-thick film; however, the perimeter of the film (outer 1-mm edge) was much thicker and was removed with a razor blade. Uniform films of 0.1–4 μm were prepared by adjusting the polymer solution concentration or the volume of solution added to the quartz plate. Profilometry of the quartz plates was done with a Sloan Dektak IIA. After removal of the outer edge the remaining film had a uniform thickness ± 20%.

Polymer degradations were done in a Mettler TG 50 thermobalance purged with a steady flow of helium (400 cm^3/min). Mass spectral analysis on the evolved gases was done with the TGA interfaced to a HP 5970A mass spectrum analyzer.

Molecular weights were determined by GPC using PMMA standards.

Acknowledgment. Andrew H. Janowicz kindly provided samples of vinyl-terminated PMMA. Al Mical chromatographed the polymer samples, and Ralph Fuller did GPC analysis. Conversations with Gregory T. Dee and William Farneth were very useful to me. Ed Lipka provided excellent technical assistance.

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Kinetics of Exchange between Adsorbed and Free Polymers at a Solid/Liquid Interface

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ABSTRACT: Adsorption of polystyrene on silica was performed at 25 and 35 °C in carbon tetrachloride. The adsorption isotherm displays two distinct regions: a plateau at low concentration, followed by a region where the adsorption amount increases steeply with the solution concentration. Radioactive ^3H labeled polymers enabled us to measure, in both regions, the intrinsic self-mobility of the polymers at the interface at constant chemical composition. As previously reported, surface molecules exchange very slowly with solution molecules. The kinetic properties are, however, very different in both regions of the isotherm. In the plateau region, fluxes can be expressed in terms of one relaxation time, whereas in the zone of high adsorption, the interfacial exchange of labeled and nonlabeled polymers cannot be characterized by one kinetic constant. The dynamical properties are connected with the specific conformational properties of polymer layers in both regions.

Introduction

The formation of an adsorbed polymer layer and its desorption raise many questions: when the bare solid surface is exposed to a polymer solution, how does the coverage increase with time? Can polymers exchange between surface and bathing solution fast enough so that thermodynamic equilibrium is rapidly established? How are kinetic and conformational properties related?

Different experimental approaches have been attempted to characterize some of these points. The main observations relative to the desorption of polymers are the following: polymer desorption is promoted by changing some parameters of the system such as temperature, solvent, pH, etc. or by using monomeric or polymeric displacers of different nature or of the same nature but of different size.[1-7] In these experiments, the adsorption equilibrium was, however, always modified and information on the intrinsic mobility of polymer species in the adsorbed state cannot be obtained.

Recently, we have used a method in which preliminary adsorption of radioactively labeled polymers was carried out, the surface then being exposed to a solution of unlabelled polymers.[8] In this way, flux measurements of labeled polymers from the surface to the solution can be measured at chemical equilibrium, and the mean time spent by a polymer at the interface, which characterizes its self-mobility in the adsorbed state, is obtained. In a systematic study of polyacrylamide adsorbed in aqueous media onto modified silica, we found that surface molecules exchange very slowly (on the laboratory time scale) with solution molecules. A metastable equilibrium is then reached in which solution is replaced by pure (or nearly pure) solvent. These kinetic aspects were analyzed from the theoretical viewpoint by de Gennes in several reports.[9,10] In this paper, we present in the same context kinetic data on the rate of exchange of labeled polystyrene adsorbed in carbon tetrachloride on silica. The polystyrene/carbon tetrachloride system is familiar in adsorption studies of polymers.[11-13] However, aerosil was most often used as sorbent. This is a pyrogenic silica which develops a large specific surface area but has siloxane and silanol groups on its surface which have different thermodynamic affinities toward the styrene ring.[12-15] Moreover, the aerosil grains are complex assemblies of elementary spheres and are not suitable models for adsorption at plane interfaces.[16] The sorbent we used is a nonporous, spherical, fully hydrated silica which bears only hydroxyl groups on its surface. In that respect, it is a better model for the study of adsorption in the presence of interacting surface sites.[17]

Experimental Section

Materials. (a) Polymer. Radioactive techniques proved useful to measure the amount of polymer adsorbed on metal surfaces.[18] In order to synthesize unlabeled polystyrene and radioactively labeled polystyrene having the same macromolecular characteristics, we prepared, by radical polymerization of styrene in the presence of traces of acrolein, a statistical copolymer of styrene and 0.2% acrolein. After purification, unlabeled polymer