pressure of 30 mN/m, pH 4.0, responding to the chain length (m) of PEG in the subphase. It is clearly seen from Figure 3 that, except for the case of PEG ($m = 4$), the area decreases systematically with increasing m up to around $m = 50$, beyond which the area is independent of m. Furthermore, the chain length of PEG, $m = 50$, at the inflection point in Figure 3 is in agreement with the chain length of the PMAA segment of 1. These results imply that a cooperative interaction between the PMAA chain of 1 and the PEG chain is enhanced with increasing m up to $m = 50$. The interesting match between n of the amphiphile 1 and m of the PEG in the subphase is considered due to the formation of the most compact coil conformation of polymer complexes at $m \geq n$. Such a compactness of the polymer complex reduced the molecular area at the air-water interface.

In conclusion, the present paper provides the first example of the chain-length relation for interpolymer complexation by a PMAA-based amphiphile at the air-water interface. This phenomenon was attained due to a combination of the amphiphilic character and the chain-length responsive character of 1. Attempts to reveal the chain-length relationships in a multilayer state are now in progress.

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(7) The structure of 1 was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Average chain length of PMAA segment in 1 was estimated by a potentiometric titration with aqueous NaOH solution.

(8) The PEGs with average molecular weights ($\bar{M}_n$) of 200, 300, 1000, 1500, 2000, 3400, and 8400 were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Polydispersities of these PEGs ($\bar{M}_w/\bar{M}_n$) were in the range from 1.1 to 1.3.

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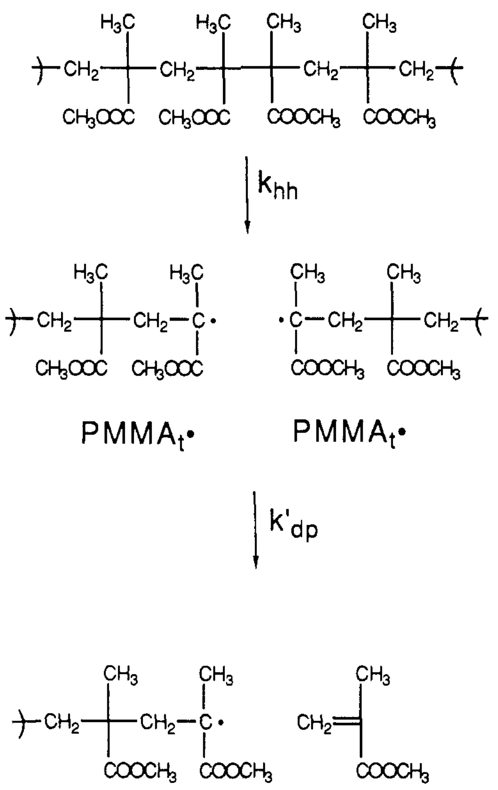
Thermal Degradation of Poly(methyl methacrylate). 3. Polymer with Head-to-Head Linkages[†]

Introduction. We have prepared PMMA in which each chain contains one head-to-head bond (PMMA-HH) using group-transfer polymerization.[1,2] We have compared the thermal degradation of PMMA-HH with PMMA-H (saturated PMMA, which contains no inherent weak links). For polymers with DP > 200 the thermal degradation of PMMA-HH and PMMA-H are similar, indicating that the head-to-head bond is having little effect under the experimental conditions. However, the degradation of DP < 100 PMMA-HH is more facile than the degradation of similar PMMA-H. Our results suggest that a large cage recombination effect, probably due to the high viscosity of the polymer melt, reduces the effective rate of head-to-head bond scission. We believe this is the first direct determination that cage recombination influences the thermal degradation of polymers.

Scheme I



Free radically polymerized PMMA thermally degrades in two or three distinct steps.[3,4] The most stable fraction of free radically polymerized PMMA (PMMA-H) contains no unsaturated end groups or main-chain head-to-head bonds, and the initiation step is a random scission.[3-8] Although it is accepted that random main-chain scission (rather than side-chain scission) initiates degradation, this point is not yet established.

A less stable fraction of free radically polymerized PMMA contains a double bond in the end group.[5,6,9-11] Double bond terminated PMMA (PMMA=) is formed simultaneously with PMMA-H by disproportionation termination of propagating radicals. It is believed that facile homolytic bond cleavage β to the terminal double bond leads to PMMA= degradation. However, we have demonstrated that degradation of PMMA= occurs by an efficient chain-transfer process in which the end group reacts with a radical to form an active chain end, which can depolymerize.[11]

The importance of head-to-head linkages in PMMA thermal degradation has been considered by a number of workers.[4-6] During MMA free-radical polymerization, PMMA chains with head-to-head bonds (PMMA-HH) are formed by coupling termination of the propagating radicals. It has been proposed that up to 28% of PMMA radicals terminate by coupling and that the PMMA-HH formed is less stable than PMMA=.[4] It is assumed the head-to-head bond is an inherently weak link so that PMMA-HH will degrade by the mechanism shown in Scheme I. Initial studies on the thermal degradation of oligomers containing head-to-head linkages indicated that PMMA-HH is less stable than PMMA=;[5] however, recent results have suggested that PMMA-HH is more stable than PMMA=.[6]

Results and Discussion. Figures 1 and 2 compare the rate of MMA appearance as a function of temperature when PMMA-H (DP$_0$ = 61, 193, and 1250) and PMMA-

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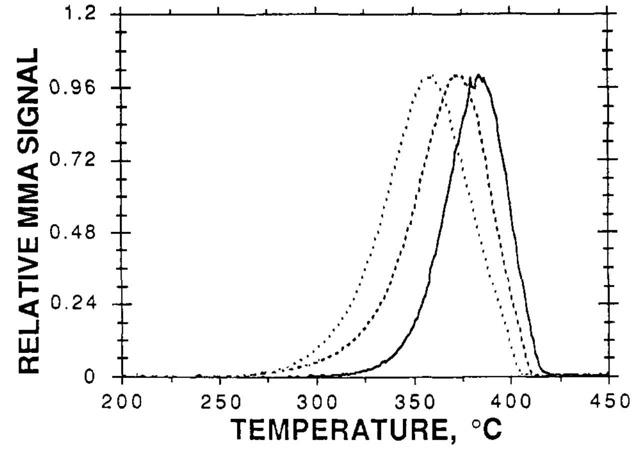

Figure 1. Appearance of MMA from thermal degradation of PMMA-H: $\mathrm{DP}_0 = 61$ (—), 193 (- - -), 1250 (···). 1–1.5-μm-thick samples heated at 20 °C/min.

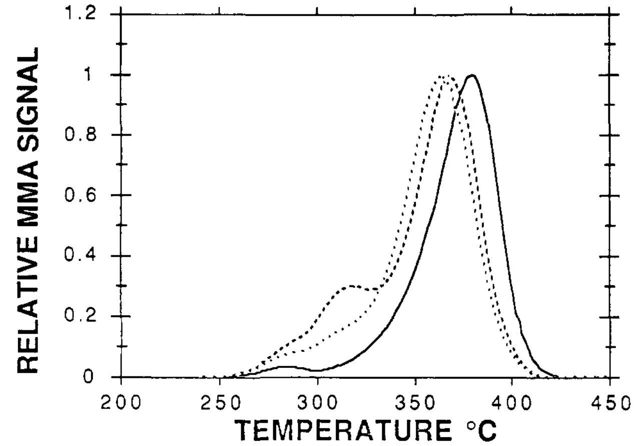

Figure 2. Appearance of MMA from thermal degradation of PMMA-HH: $\mathrm{DP}_0 = 119$ (—), 379 (- - -), and 664 (···). 10–15-μm-thick samples heated at 20 °C/min.

HH (DP_0 = 119, 379, and 664) samples are heated at 20 °C/min. Consistent with the accepted random scission mechanism, PMMA-H degradation temperatures are inversely proportional to DP_0.[12] With PMMA-HH, Figure 2, the head-to-head bonds cause some degradation below temperatures expected for a random scission initiated process. However, the bulk of PMMA-HH degradation appears random scission initiated as if the head-to-head bond is having little effect on the rate of degradation.

Isothermal studies also suggest the head-to-head bond has little effect when $\mathrm{DP}_0 > 200$. Isothermal degradation of PMMA-HH with $\mathrm{DP}_0 = 300$ at 320 °C leads to 15, 26, 44, and 61% mass loss after 15, 30, 60, and 120 min, respectively. The initial rate of mass loss is approximately first order and only twice that expected for a random scission initiated process (assuming $E_a = 62.4$ kcal/mol and $A = \mathrm{DP} \times 2 \times 10^{16}\ \mathrm{s}^{-1}$ for the random scission process).[7] Furthermore, comparison of molecular weight distributions of PMMA-HH with $\mathrm{DP}_0 = 300$ before and after partial degradation shows a gradual shift toward lower molecular weight consistent with a random scission initiated process.[12]

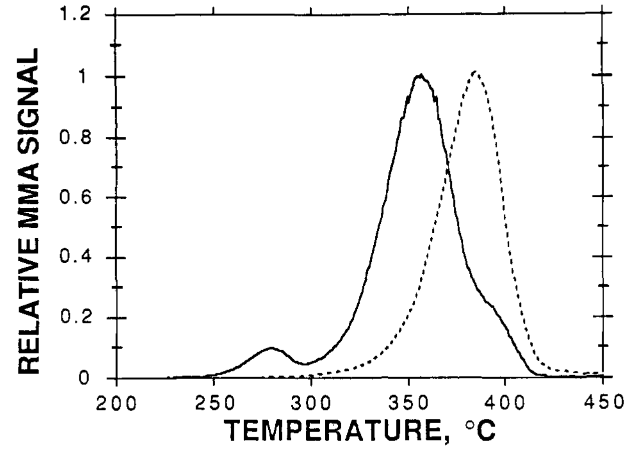

Figure 3. Appearance of MMA from thermal degradation of PMMA-HH (—, $\mathrm{DP}_0 = 57$) and PMMA-H (- - -, $\mathrm{DP}_0 = 61$). 5-μm-thick samples heated at 20 °C/min.

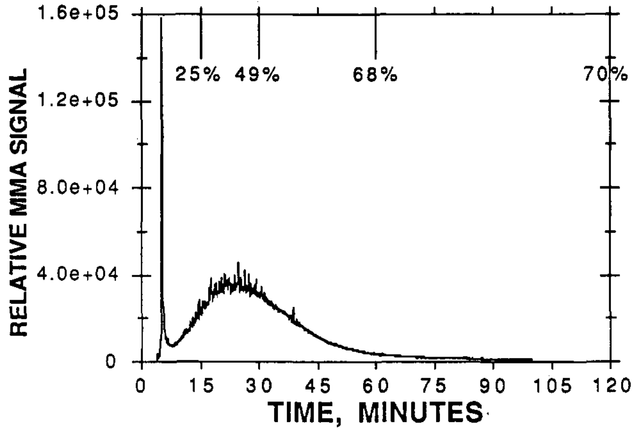

Figure 4. Appearance of MMA during isothermal degradation of PMMA-HH ($\mathrm{DP}_0 = 46$) at 320 °C. Initial sample thickness > 100 μm.

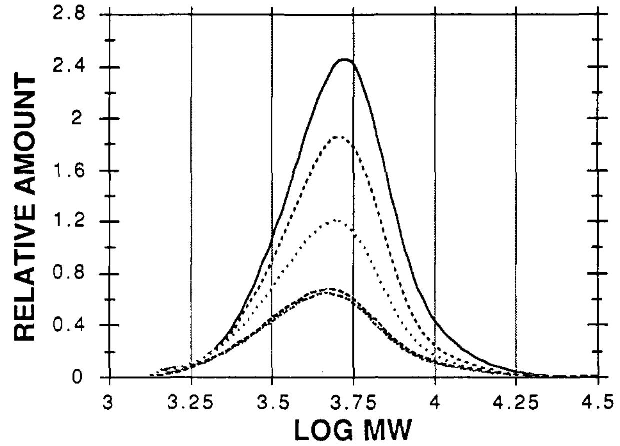

Figure 5. Molecular weight distributions for PMMA-HH ($\mathrm{DP}_0 = 46$) after 0, 25, 48, 68, and 70% isothermal degradation at 300 °C. Initial sample thickness > 100 μm.

In contrast to the results observed with PMMA-HH when $\mathrm{DP}_0 > 200$, Figure 3 compares the rate of MMA appearance as a function of temperature when PMMA-H ($\mathrm{DP}_0 = 61$) and PMMA-HH ($\mathrm{DP}_0 = 57$) samples are heated at 20 °C/min. In this case, PMMA-HH degrades at a considerably lower temperature than PMMA-H. Isothermal degradation of PMMA-HH with $\mathrm{DP}_0 = 46$ leads to 25, 49, 68, and 70% mass loss after 15, 30, 60, and 120 min, respectively. Mass loss is >150 times faster than expected for a random scission initiated process (to 25% degradation, vide supra). Figure 4 shows the appearance of MMA during this isothermal degradation. The degradation process is complicated (certainly not first order), actually showing a considerable rate increase as degradation proceeds.

The effect of degradation on the molecular weight distribution of PMMA-HH is different for $\mathrm{DP}_0 < 100$ and $\mathrm{DP}_0 > 200$ polymer. Figure 5 compares molecular weight distributions of PMMA-HH with $\mathrm{DP}_0 = 46$ before and after partial degradation. The small shift in molecular weight distribution is consistent with degradation initiated by head-to-head bond cleavage (Scheme I).

We do not yet know the cause for the observed rate increase during isothermal degradation of PMMA-HH with $DP_o = 46$ (Figure 4). We also observe unexpected thickness effects on the degradation of PMMA-HH samples. The degradation rate often increases as the sample thickness decreases. It is possible that main-chain head-to-head scission is more efficient near a surface than in the bulk polymer melt; however, these details will require further study.

Conclusion. We have demonstrated that incorporation of "weak" head-to-head bonds in a PMMA chain can reduce the polymer degradation temperature by promoting facile homolytic scission of the chain. However, when $DP_o > 200$, the apparent rate of main-chain scission is greatly reduced by extensive cage recombination that overwhelms the effect of head-to-head bonds.

Many proposed (accepted) polymer degradation mechanisms anticipate an initial main-chain scission in the first step. Our results suggest that main-chain scissions will be kinetically inhibited relative to side-group or chain-end cleavage. Initial cleavage of side-chain groups followed by β-scission might initiate polymer degradation when the bond dissociation energies for side-group and main-chain scissions are similar.

Future studies will address the surface-to-volume effects on PMMA-HH thermal degradation. We also plan to prepare PMMA-HH where the head-to-head bond is at the chain end. We anticipate that chain-end head-to-head bonds will not undergo as much cage recombination as internal head-to-head bonds.

Experimental Section. Experimental procedures used to monitor PMMA thermal degradation have been reported previously.[11]

PMMA-HH was prepared by group-transfer polymerization[1,2] using the difunctional initiator 1,4-bis(trimethylsiloxy)-1,4-dimethoxy-2,3-dimethylbutadiene (I). The initiator, I, is prepared by standard procedures from 2,3-dimethyl dimethylsuccinate, lithium diisopropylamine, and trimethylsilyl chloride.[13] The initiator synthesis gives three regioisomers of I (*Z,Z*; *E,E*; and *E,Z*), which could be separated chromatographically; however, a mixture of the three isomers was used for polymer initiation. Both the rate of polymerization (slow) and the resultant MW distributions ($M_w/M_n \sim 1.3$) indicate that the rate of initiation (k_i) is slower than the rate of propagation (k_p) for these conjugated difunctional initiators. The presence of head-to-head bonds in the polymer is dictated by the established mechanism of group-transfer polymerization.[1,2,14,15]

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Concerning the Miscibility of PVC–PVAc Blends

In the absence of specific interactions most homopolymer blends are immiscible. Accordingly, there has been a great deal of interest in the experimental observation of "miscibility windows" in mixtures of certain copolymers, even though binary blends of homopolymers of the various constituents are immiscible.[1-4] This has been explained on the basis of a "repulsive" interaction between the units of the copolymer.[2,5,6] For example, for a system containing a copolymer 1 comprised of two different monomer units, A and B, blended with a homopolymer 2 having monomer units, C, a Flory–Huggins free energy of mixing may be written as

$$\frac{\Delta G_M}{RT} = \frac{\Phi_1}{N_1}\ln \Phi_1 + \frac{\Phi_2}{N_2}\ln \Phi_2 + \Phi_1\Phi_2\chi_{\text{blend}} \qquad (1)$$

where χ_{blend} is given by

$$\chi_{\text{blend}} = \chi_{AC}\Phi_A + \chi_{BC}\Phi_B - \chi_{AB}\Phi_A\Phi_B \qquad (2)$$

and Φ_1 is the volume fraction of the $(A_{\Phi_A}B_{\Phi_B})_n$ copolymer, Φ_2 is the volume fraction of the homopolymer C, and N_1, and N_2 are the respective degrees of polymerization of the chains. It follows that even if χ_{AB}, χ_{AC}, and χ_{AB} are all positive, χ_{blend} can still be negative, depending upon the composition of the copolymer and the relativer magnitudes of the individual segmental interaction parameters.

While the above concept is elegant and appealing, one must question whether or not it has been truly tested experimentally. It is well established that the presence of specific favorable intermolecular interactions between the components of a binary polymer blend favors miscibility. In eq 2 this is equivalent to χ_{AC} and/or χ_{BC} assuming negative values in which case it is not necessary to invoke a "repulsion" between the different monomer units of the copolymer to obtain an overall negative χ_{blend}. For example, blends involving poly(vinyl chloride) (PVC), poly(vinyl acetate) (PVAc), and various copolymers that include a third comonomer have been the subject of detailed studies.[8-10] Although specific interactions involving the acetate carbonyl group have been identified,[7,8] the work of Shiomi, Karasz, and MacKnight[9] and Cruz-Ramos and Paul[10] results in the determination of a positive χ for interactions between PVC and PVAc segments. In their study of PVC–poly(ethylene-*co*-vinyl acetate) (EVA) blends Cruz-Ramos and Paul[10] reviewed the literature and

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