

Thermal Analyses of Graft Copolymers of Poly(Methyl Methacrylate) Main Chain with Poly(Propylene Oxide-*b*-Ethylene Oxide) Graft Chain

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SYNOPSIS

Poly(methyl methacrylate-*g*-(propylene oxide-*b*-ethylene oxide)) and poly(methyl methacrylate-*g*-(ethylene oxide-*b*-propylene oxide)), comprising chemically dissimilar sequences, exhibit intramolecular phase separation. These compositions have applications in coatings and as surface-tension modifiers. This paper presents the thermal behavior of these graft copolymers: separate samples of the homopolymer and of the grafts were also analyzed to provide comparisons. The phase behavior has been analyzed by differential scanning calorimetry and by dynamic-mechanical thermal measurements. Two glass transitions (T_g) are observed, caused by the partial incompatibility within the copolymers. The activation energy of the T_g relaxation process of the main chain is decreased by the graft chain. The influence of poly(propylene oxide-*b*-ethylene oxide) grafts on the thermal degradation of the poly(methyl methacrylate) (PMMA) main chain was studied by using thermogravimetric analysis. Pyrolysis of the graft copolymers occurs in three stages and begins on the graft chain and at a lower temperature than the pyrolysis of pure PMMA. Both the phase behavior and the thermal stability are found to depend sensitively on the composition of the copolymer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(methyl methacrylate-*g*-(propylene oxide-*b*-ethylene oxide)) and poly(methyl methacrylate-*g*-(ethylene oxide-*b*-propylene oxide)), having sequences that are chemically dissimilar, exhibit intramolecular phase separation. Their properties lead to a number of specific applications such as in coatings, surface modifiers, and as surface-tension agents. The thermal behavior of these graft copolymers were examined in separate samples of the homopolymer and in the grafts analyzed to provide comparisons. Concerning the main chain, poly(methyl methacrylate) (PMMA), prepared by the conventional free-radical method is known to be about 60% syndiotactic, and has a glass transition temperature, T_g , of about 100°C. The pure syndiotactic stereoregular form has a T_g of 115°C.

Poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) homopolymers of low molecular weight (600–4000) are known to be effective plasticizers for PMMA, reducing its modulus at low content (up to 20 wt %). These blends ease the processability of the PMMA, while reportedly retaining the homogeneity of the system.^{1,2}

The thermogravimetry of PMMA and the effect of comonomers, such as ethyl methacrylate, has been studied extensively.^{3–10} This paper evaluates the influence of poly(propylene oxide-*b*-ethylene oxide) graft chains on the thermal behavior of the PMMA main chain.

PMMA is a polymer that pyrolyzes predominantly to monomer. In PMMA prepared by anionic polymerization, the depolymerization takes place at ~ 350°C in one step initiated by homolytic and random chain cleavage.⁵ This process gives almost 100% yield of monomer. This indicates that little chain transfer occurs, as both initial radical ends rapidly unzip until they either volatilize or are lost by a number of processes, some of which are disproportionation and recombination with a second radi-

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cal, plus possible reaction with MMA (forming R-MMA).⁶

In contrast, the thermal degradation of PMMA produced by free-radical polymerization occurs in two temperature stages.⁷ At the lower temperature ($\sim 270^\circ\text{C}$), the radical chain unzipping reaction is characterized by unsaturated chain-end initiation. A higher temperature ($\sim 350^\circ\text{C}$) initiation occurs randomly along the polymer chain. The effect of initial molar mass and of the ratio of mol MMA/mol AIBN (azobisisobutyronitrile) on the nonisothermal degradation of free radically prepared PMMA has been evaluated.⁸ The curve shapes from thermal gravimetry differ for samples prepared at 60°C for mol ratios MMA/AIBN of 2.36 and 2.50. The former is more stable at lower temperatures.

PEO and PPO do not pyrolyze preferentially to produce monomer. Their degradation yields only a small amount of monomer. The degradation mechanism is similar to that of PE and PP, but the presence of oxygen decreases thermal stability.⁵ The oxidative thermal stability of PEO and of anionic surfactants such as EO/PO block copolymers have been studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).^{11,12} The heat balance is highly positive (exothermic) and the net heat release depends on the ratio of EO to PO units.

Several methods have been used to study polymer pyrolysis: techniques of thermal analysis (TGA, DSC, thermal volumetric analysis, TVA), IR, NMR, gas chromatography (GC), and mass spectrometry (MS).⁷ Particularly, GC/MS methods have been used extensively to identify the volatiles from degradation.¹³⁻¹⁸ They are specially important for the qualitative characterization of the monomers in an acrylic copolymer because of the highly reproducible GC monomer profiles observed upon pyrolysis.¹⁸

Several have studied PMMA and PEO, their blends,¹⁹⁻²⁵ and copolymers.^{2,3} Their mutual miscibility as a function of molecular weight and percent of the components has been the main subject. Blends of PMMA and PEO have been reported to be miscible for compositions containing PEO concentration of ≤ 20 wt %² and to become immiscible for PEO concentration between 25 and 50 wt %.¹ It is thus assumed that any favorable interactions between this pair are relatively weak (dipole-dipole).²⁶ Blends of PMMA and PPO have likewise been reported to be miscible for compositions containing PPO concentrations of ≤ 20 wt %.²⁷ However, where PPO is attached as a graft to the PMMA main chain, the phase separation does not occur up to a PPO concentration of ≤ 50 wt %.³

The most commonly used criterion for miscibility is the existence of a single T_g . The change in C_p at T_g may provide the least ambiguous assignment of T_g ²⁸ for the technique most used, differential scanning calorimetry. However, greater transition sensitivity can be obtained by use of dynamic mechanical methods. By resolving the stress into real and imaginary components, essentially all changes in the state of molecular motion can be measured as the temperature is scanned. Secondary transitions can also be observed. Five transitions in syndiotactic PMMA have been observed by dynamic mechanical thermal analysis (DMTA). They are reported to be: $\alpha(T_g)$, microbrownian vibration in the main chain at 125°C ; β , molecular motion of the ester pendant group (carbomethoxy) at 20°C ; β_w , at -100°C , observed only in PMMA that has absorbed water; γ , microbrownian vibration of α -methyl group at -170°C ; and the δ transition, microbrownian motion of methyl group in the pendant group (ester methyl group) at -269°C .²⁸⁻³¹ For semicrystalline PEO of high M_w , α and β peaks are reported at -65 and -140°C , respectively. For amorphous PPO of high M_w , α and β peaks are reported at -62 and -163°C , respectively.³¹

The energy associated with transition processes can be calculated by using the area under the peak of the modulus vs. temperature curve in dynamic-mechanical tests. The activation energy for the relaxation can be derived from loss peak position at different frequencies by using an Arrhenius plot, where H is the loss peak frequency at absolute temperature T :

$$\log H = \log A - \frac{E_a}{2.3R} \cdot \frac{1}{T} \quad (1)$$

where E_a , activation energy; R , gas constant; A , a constant. A plot of eq. (1) is useful for considering the temperature dependence of relaxation processes.

The activation energy of the PMMA T_g α -relaxation has been reported to be 80 kcal/mol, and for the β -relaxation between 17 and 30 kcal/mol.³¹

EXPERIMENTAL

Thermogravimetric Analysis and Differential Scanning Calorimetry

Data were collected on a Perkin Elmer TGS-2 and DSC-4, both interfaced with a TADS data station and a System 4 microprocessor controller. All temperature scans were carried out under 0.1 L/min nitrogen flow. The scanning rate was $20^\circ\text{C}/\text{min}$ and

weight loss (%) or heat flow were registered as a function of temperature.

Pyrolysis-Gas Chromatography/Mass Spectrometry

Analyses were done with a Hewlett Packard (HP) Pyroprobe HP 18580A (with Pt ribbon) coupled to a gas chromatography HP 5890A utilizing a 5970 Mass Selective Detector operated at 70 eV.

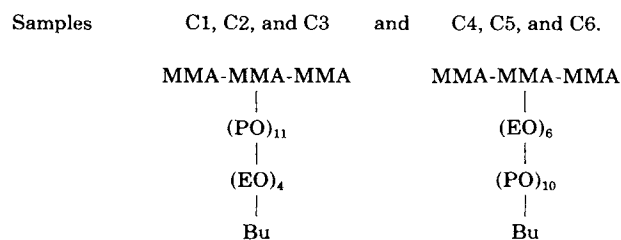
All pyrolyses were conducted with the pulse rate control in the off position. The final set temperature was 800°C. Less than 30 s were required for the sample chamber to assume block temperature.

The gas chromatograph consisted of an HP-5 fused silica capillary column 2.5-m \times 0.21-mm i.d. with a 0.11-m film thickness, initially heated to 40°C (2 min) and ramped to 280°C at 20°C/min. The injection port and transfer line temperatures were 270°C and 280°C, respectively.

The mass spectra obtained were signal averaged with a subsequent background subtraction.

Samples were prepared in two different ways to obtain mass spectra: 1 mg of polymer was dissolved in 1 mL of chloroform and this solution was used for analysis by Py-GC-MS. Gases from TG decomposition were trapped in toluene and analyzed by GC-MS.

Two different graft copolymers were analyzed by TGA and DSC:



The graft copolymers were obtained by free-radical polymerization, as discussed previously.³² The ratio of monomer/mol AIBN was 330. The samples were dried in a vacuum oven and kept in a desiccator because moisture complicates analysis. The characterization data for the graft copolymers studied, identified as C1-C6, are summarized in Tables I and II.

The methacrylate polymers used for comparison, were obtained from commercial sources: PMMA, Sp2 Scientific Polymer Products, Inc.: M_w , \sim 75,000 (GPC); inherent viscosity 0.45. PEMA, Aldrich: M_w 340,000; M_n 126,000. Poly(*tert*-butyl methacrylate), Aldrich: d , 1.022; T_g , 107°C; Poly(*N*-amyl methacrylate), Polysciences.

A DuPont Thermal Analysis System, the differential scanning calorimeter 10 (DSC 10) was used for T_g analysis and heat capacity increment (ΔC_p) at T_g . Thermal scans were recorded between -100 and 150°C at a heating rate 20°C/min. T_g was taken as the inflection point of the C_p (specific heat discontinuity at T_g) and the ΔC_p 's were averaged for two runs (Table II).

Dynamic mechanical measurements were carried out with a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (PL-DMTA) operated in the two point bending mode with a strain amplitude of 60 μ m (strain setting of $\times 4$), under dry nitrogen from -120 to 150°C, and frequency range of 0.3-10 Hz at a heating rate of 2°C/min. The samples were prepared in a vacuum press at 150°C and the thickness of the films was about 0.6 mm.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 compares the TGA curves of PMMA with that for its grafts, Bu(EO)₄(PO)₁₁OH and

Table I Characterization of Poly(Methyl Methacrylate-*g*-[Propylene Oxide-*b*-Ethylene Oxide])

Copolymer	Graft Chain	Graft Chain (wt %) ^a	\bar{M}_n ^b	\bar{M}_w ^c
C1	Bu(EO)(PO)	12	43700	114000
C2	Bu(EO)(PO)	15	65700	123000
C3	Bu(EO)(PO)	18	80800	175000
C4	Bu(PO)(EO)	11	78400	131000
C5	Bu(PO)(EO)	14	84500	147000
C6	Bu(PO)(EO)	20	67300	150000

^a Determined by ¹H NMR spectroscopy.

^b Determined by VPO in toluene at 25°C.

^c Determined by GPC in tetrahydrofuran using polystyrene standards.

Table II Thermal Properties of Graft Copolymers

Sample	Graft Chain				Main Chain	
	Graft (wt %)	T_g (°C)	ΔC_p (J/g deg ⁻¹)	ΔC_p (J/g deg ⁻¹)	T_g (°C)	ΔC_p (J/g deg ⁻¹)
PMMA	—	—	—	—	115	0.50
Bu(EO)(PO)OH	—	-71	—	—	-36	—
C1	12	10	0.36	3.00	114	0.50
C2	15	5	0.46	3.09	113	0.67
C3	18	3	0.43	2.39	106	0.67
Bu(PO)(EO)OH	—	-73	—	—	-35	—
C4	11	16	0.40	3.66	110	0.68
C5	14	14	0.40	2.88	106	0.70
C6	20	12	0.44	2.22	97	0.59

T_g 's believed reliable, $T \pm 1.0^\circ\text{C}$. Heating rate = $20^\circ\text{C}/\text{min}$.

$$C_p = \frac{E_q}{B} \times \frac{60 \text{ s}}{\text{min}} \times \frac{1000 \text{ mg}}{\text{g}} \times \frac{1}{W}$$

where C_p = heat capacity (J/g deg⁻¹); E = cell constant (dimensionless); q = heat flow (W); B = scan rate (°C/min); W = sample weight (mg).

Bu(PO)₁₀(EO)₆OH. The results are consistent with the literature:¹¹⁻¹² namely, PMMA is stable below ~ 250°C; above this temperature the degradation, that is, depolymerization takes place and once initiated, the macroradical unzips completely for this free-radically polymerized MMA. Indeed, only MMA was observed from the PMMA pyrolysis. The decomposition of EO/PO block copolymer begins

at a lower temperature, ~ 160°C, but it occurs over a temperature range, with no more than 10% volatilizing up to 370°C. The small difference in Figure 1 between the two EO/PO block copolymers is related to the ratio EO/PO units. Since PEO is more stable than PPO,⁴ the block copolymer of higher EO/PO ratio is more stable at lower temperatures.

Figure 2 compares the reproducible TGA curves

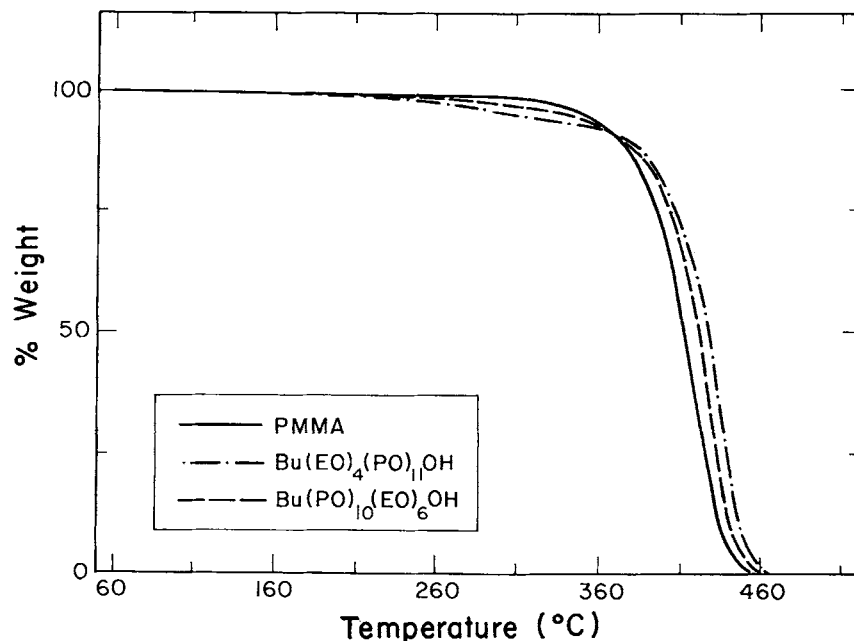


Figure 1 Thermogravimetric analysis of PMMA homopolymer and the two PPO/PEO block copolymers (heating rate: $20^\circ\text{C}/\text{min}$).

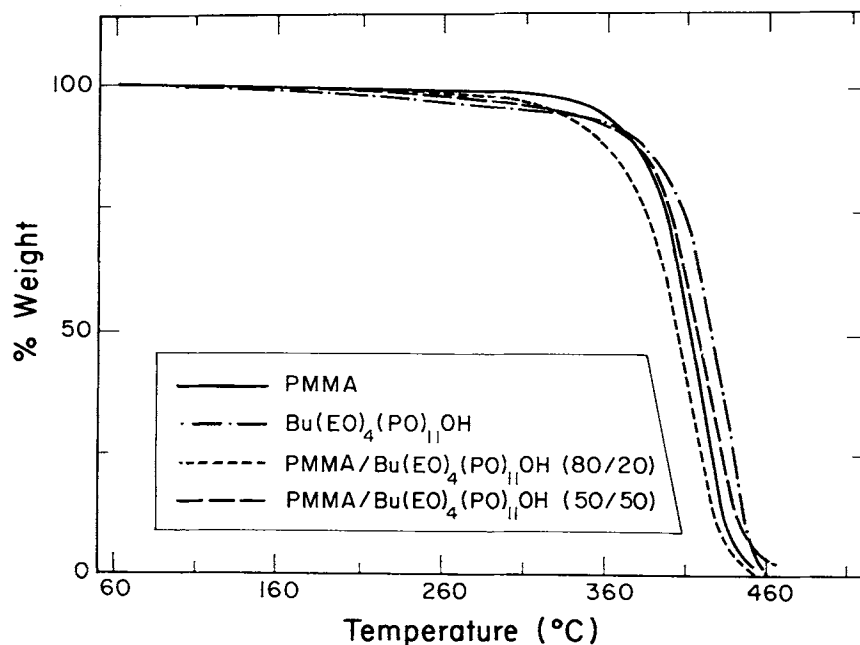


Figure 2 Thermogravimetric analysis of blends of PMMA and PPO/PEO block copolymer (heating rate: 20°C/min), repeated from Figure 1 plus curves for two of their physical blends.

of two physical blends with the pure components previously shown in Figure 1. These 15-mg blends were prepared by mixing PMMA (powder) and $\text{Bu}(\text{EO})_4(\text{PO})_6\text{OH}$ (fluid) in the two ratios shown in Figure 2. The shape of the curves shows the deg-

radation processes characteristic of each polymer constituent. No interaction is evident.

However, the TGA of the graft copolymer TGA curve differs from that of the physical blend (Fig. 3). A reaction at the main and graft chain link is

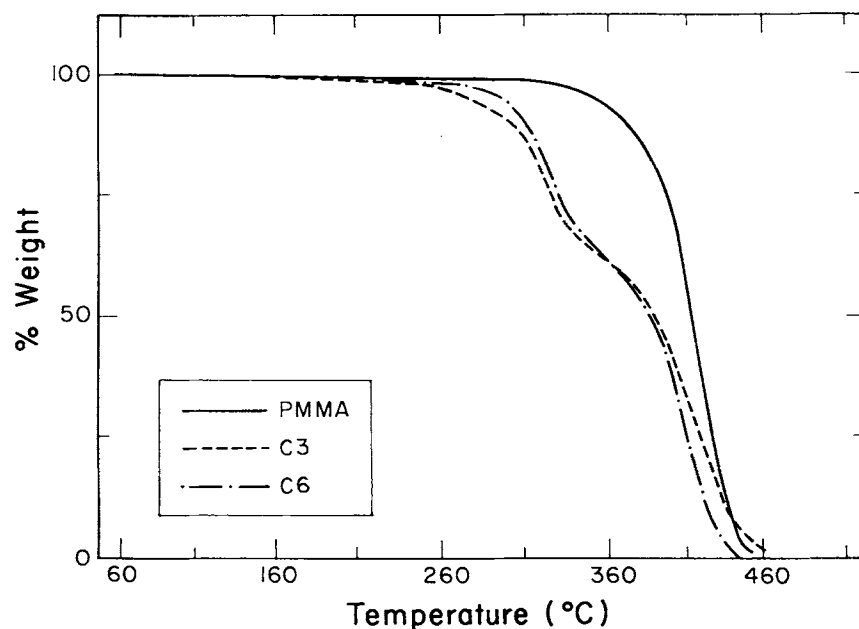


Figure 3 Thermogravimetric analysis of PMMA homopolymer and graft copolymers (C3 and C6) (heating rate: 20°C/min).

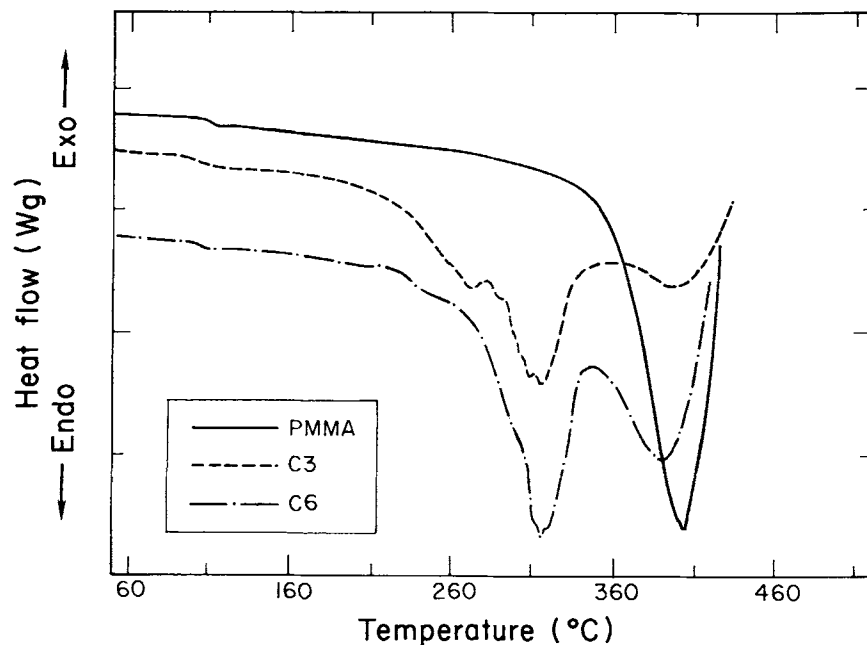


Figure 4 Differential scanning calorimetry of PMMA homopolymer and graft copolymers (C3 and C6) (heating rate: 20°C/min).

thus evident. The weight loss of graft copolymer begins at a lower temperature than for PMMA, as in the blend, and it occurs in three stages. These three stages, as well as their endothermic character, are reflected in the TGA and the open cup DSC curves,

as shown in Figures 3 and 4. The first stage is related to the short PMMA chains in the graft copolymer (Table I). Stage 1 depends on heating rate and tends to merge at a higher heating rate.

Figure 5 shows the TGA curves of PMMA, the

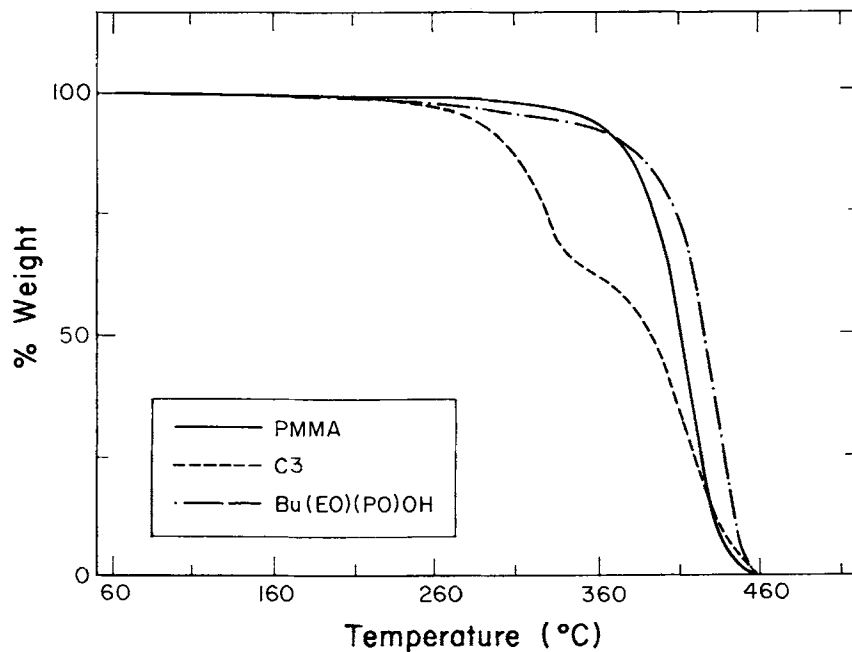
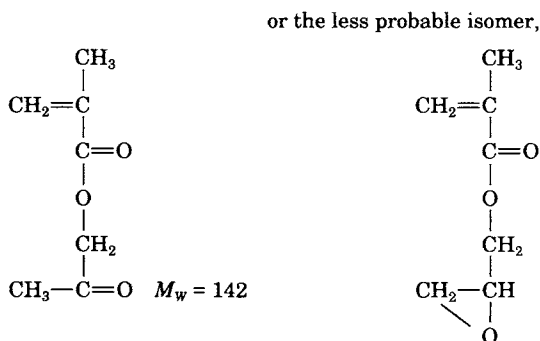


Figure 5 Thermogravimetric analysis of C3 graft copolymer and PMMA homopolymer (main chain) and separate PPO/PEO block copolymer (graft chain).

graft copolymer C₃, and the graft itself, the C3 copolymer. Figure 5 suggests that the pyrolysis begins on the graft chain and the third slope is caused by PMMA pyrolysis. Results obtained from GC/MS support this conclusion concerning the thermal susceptibility of the graft chain, and indicates an overlap of the PMMA pyrolysis.

The products collected in toluene from the second slope of the C3 TG decomposition were analyzed by GC/MS. It was not possible to catch all the gases evolved from the degradation, but the results aid understanding. By analyzing the mass spectra of the product detected at 7.736 min by GC, it is suggested that the C3 thermal decomposition (20°C/min; N₂ flow = 0.1 L/min) yields species with the following structure:



It is important to consider the relation between the mass spectra and the structures suggested above.

The mass spectra for below m/z 100 is similar to that of PMMA. So, it may be inferred that this component is pure MMA. There are two points against the possibility that this product is MMA dimer or other products. When pure PMMA is decomposed in the same way and analyzed under the same conditions, only monomer is observed. Snyder¹⁸ studied oxidative pyrolysis to characterize several PMMAs. The results he obtained on PMMA (at specific experimental conditions) show peaks at m/z 141, the dimer (M_w 200) less a COOCH₃ group (M_w 59) and m/z 115, 127, and 155 caused by other molecular cleavage modes.

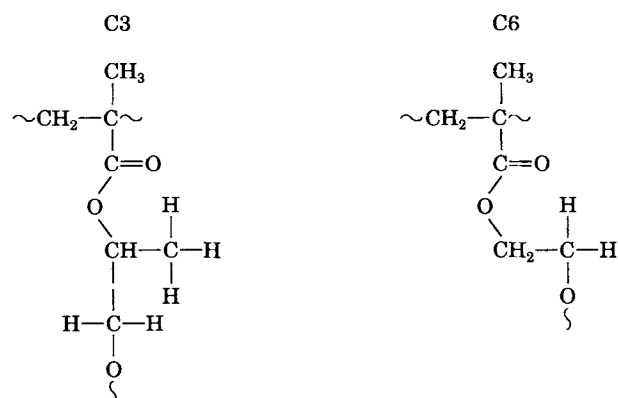
The presence of isotopes of known natural abundance makes possible a useful and simple method for deducing the elemental composition of mass ions. The probability that an ion of a specific number of C¹² atoms will contain one C¹³ is 1.1%.³³ The number of carbon atoms can be calculated by using the relative abundance of the peaks at m/z 142 and 143 and the equation $(A + 1)/A \times 100 = \#C \times 1.1$. Since the relative abundance of the peaks at m/z 142 and 143 was 100 and 70, respectively, the value found

for number of carbon atoms is 6.4. It is therefore expected that this compound ion contains 6 or 7 carbon atoms.

The pyrolysis products with GC retention times > 16 min are difficult to interpret, probably because of radical recombination in the TGA pan, even for small samples. Recombination in the TGA pan was confirmed when the chromatograms were compared for the material left in the pan (after stopping TGA of C3 copolymer at 350°C) and of the C3 copolymer pyrolyzate. Pyrolysis of the residue results in a larger number of products. The mass spectrum of the C3 copolymer shows that some ether and aldehyde compounds form from the PEO/PPO pyrolysis in addition to the MMA from the PMMA.

A related analysis was carried out by GC/MS using the products collected in toluene from the third slope of C3 TG decomposition. This analysis shows that the major product is indeed MMA (> 80%). No other significant peak was observed.

By comparing the TGA of graft copolymers C3 and C6, a small difference can be observed (Fig. 3). The greater instability of C3 at lower temperature is caused by the greater instability of its graft chain (Fig. 2). The difference between the two plateaus of C3 and C6 is related to the reaction at the ester groups. The decomposition mechanism of PMAs such as poly(ethyl methacrylate) (PEMA) and poly(*tert*-butyl methacrylate) (PTBMA) have been reported.^{7,34} They suggest that the reaction occurs by way of a six-membered ring transition state, which for C3 and C6 is represented by:



In both cases, the reaction proceeds by a mechanism involving interaction between the ester carbonyl group and the hydrogen atoms on the β carbon atom of the next ester group. Propylene oxide contains five hydrogen atoms on two β carbons and ethylene oxide has only two. Figure 6 shows that the TGA curves of different higher PMAs all exhibit

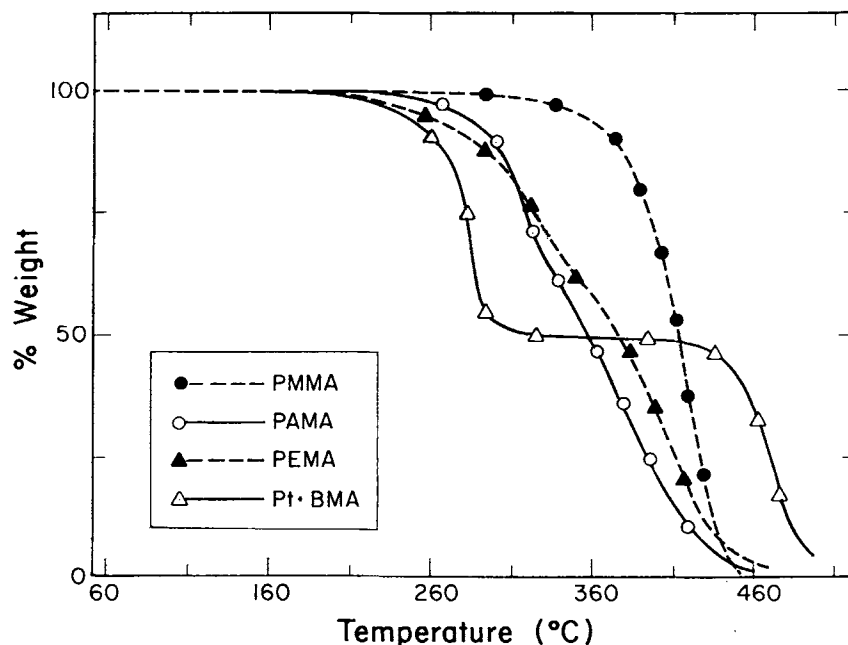


Figure 6 Thermogravimetric analysis of polymethacrylates: PMMA-poly(methyl methacrylate); PAMA-poly(*n*-amyl methacrylate); PEMA-poly(ethyl methacrylate); PTBMA-poly(*tert*-butyl methacrylate).

more than one slope. PTBMA, which has the highest number of hydrogen atoms on β carbons, results in less stability at lower temperature and a marked plateau between the two last stages. The difference observed in TG curves of graft copolymers is therefore considered to be related to the reaction at the ester pendant group of the MMA main chain.

The influence of the composition on the pyrolysis of the graft copolymer was further analyzed. The results seem to be related more to the molecular weight (Table I) than to the composition (in the range analyzed). Indeed, the thermal stability of graft copolymers increases with the molecular weight.

Calorimetric Analysis

DSC results on the graft copolymers are shown in Table II. The PPO-*b*-PEO block copolymers exhibit no melting and present two low T_g 's, probably caused by the influence of the end-group (butyl) interactions in the thermodynamics of mixing.^{35,36} All graft copolymers investigated show two T_g 's, just one for the graft and one for the PMMA. That means also that the graft copolymers are not mutually miscible, even when the copolymer contains only 11 wt % of the graft chain, in contrast to the corresponding miscibility of corresponding physical blend of main chain PMMA and graft.

Polymer-polymer miscibility requires that the Gibb's free energy for mixing be negative:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

and that the second derivative of the free energy with respect to some composition variable, X , be positive:

$$(\partial^2 G_m / \partial X_i^2)_{T,P} > 0.$$

The inequality requires that the energy-composition diagram be concave downward.³⁷ The system is immiscible because of its intermolecular energy dissimilarities.

The phase behavior as a function of temperatures was investigated. The two T_g 's become closer, but no single T_g was observed on reheating even after quenching at temperatures of decomposition.

The two T_g 's observed for all graft copolymers are related to the two phases present, the higher T_g is for the phase rich in PMMA, and the lower for the phase rich in PEO-*b*-PPO. For all graft copolymers, the two T_g 's are located between -70°C (lower T_g of PEO-*b*-PPO) and 115°C (T_g of PMMA) (Table II). The results show that the T_g 's for the copolymers, which have the Bu(PO)(EO) graft, are closer than the copolymers, which have the Bu(EO)(PO) graft, and, indicates higher compat-

ibility in the system where Bu(PO)(EO) was used as the graft chain.

Intermolecular forces and chain packing affect motions in the glassy state. In this case, the soft segment (graft chain) has the effect of decreasing the T_g of the PMMA phase. T_g decreases from $\sim 115^\circ\text{C}$ (pure PMMA) to 95°C (C6 copolymer) (Table II). On the other hand, the PMMA (more rigid main chain) has the effect of decreasing the mobility of the PEO-*b*-PPO, increasing the T_g of this phase. The variation of the chain mobility of each phase as a function of composition can be observed by measuring the change in heat capacity at T_g (ΔC_p) that increases in both phases for higher weight percent of graft chain (softer segment).

Dynamic Mechanical Analysis

Dynamic mechanical methods, by resolving the stress into real and imaginary components, detects viscoelastic behavior. When a polymer is subjected to a sinusoidal stress at constant frequency while

programming the temperature, molecular relaxations may be observed by measuring the out-of-phase strain component. When the average relaxation time of molecular motions in the polymer becomes comparable to the timescale of measurement, maxima are observed in the loss component of the stress, because of dynamic mechanical energy lost as heat.³¹ In these analyses, all results for PMMA agree with the literature.³¹ As expected, two readily apparent relaxations are assigned to the onset of chain motions associated with the T_g (125°C , at 1 Hz) and the β -relaxation (21°C , at 1 Hz), which arises from the hindered rotation of the carbomethoxy group about the carbon-carbon bond linked to the main chain.

The activation energies, E_a , calculated from an Arrhenius plot ($\log H$ vs. E_a/RT), are ~ 100 kcal/mol and ~ 33 kcal/mol, respectively, for the T_g and β -relaxations of PMMA.

Figure 7 shows the temperature dependencies of the storage moduli (E'), loss moduli (E''), and the loss factor ($\tan \delta$) at multifrequency scans (0.33,

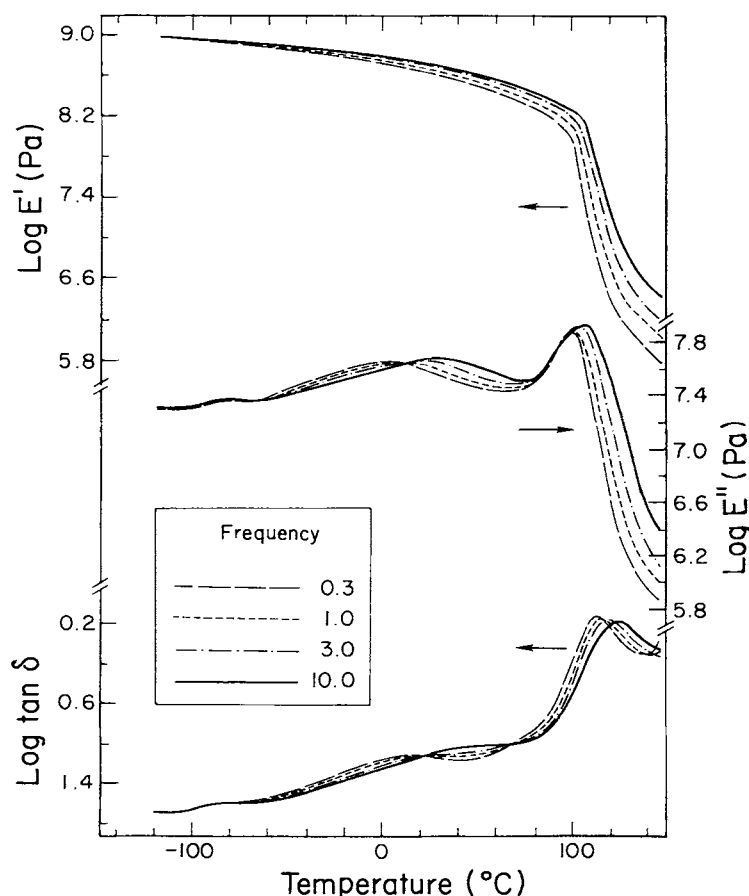


Figure 7 Multifrequency thermal scan of storage E' and loss E'' moduli for C3 graft copolymer.

Table III Dynamic Mechanical Measurements, Transition Temperatures of Graft Copolymers

Sample	Graft Chain			Main Chain	
	Graft	Graft (wt %)	T_g (°C)	T_g (°C)	E_a^a (kcal/mol)
PMMA	—	—	21 ^b	125	100
C1	Bu(EO)(PO)	12	26	118	96
C2	Bu(EO)(PO)	15	25	116	94
C3	Bu(EO)(PO)	18	23	113.5	84
C4	Bu(PO)(EO)	11	25	115	78
C5	Bu(PO)(EO)	14	18	113.5	78
C6	Bu(PO)(EO)	20	16	111	75

$\tan \delta$, damping peak; 1 Hz; 2°C/min.

^a Activation energy related to higher T_g .

^b Secondary β -transition of PMMA.

1.0, 3.0, and 10 Hz) for the C3 graft copolymer [18 wt % of Bu(EO)(PO)]. Three relaxation processes are observed. Two are considered to be a T_g . The relaxation around 100°C is the T_g of the phase rich in PMMA and the relaxation around 20°C is related to the T_g of the phase rich in graft chain. Table III shows the graft chain content influence on T_g 's. As in DSC, a clear decrease in T_g with graft content is observed because of the higher mobility introduced by the soft segment (graft chain). Figure 8 shows an Arrhenius plot of the frequency as a function of the reciprocal of the absolute temperature for the α (T_g) peak maxima. The larger activation energy reflects the greater restriction of the molecular mobilities involved in a relaxation process to be activated.

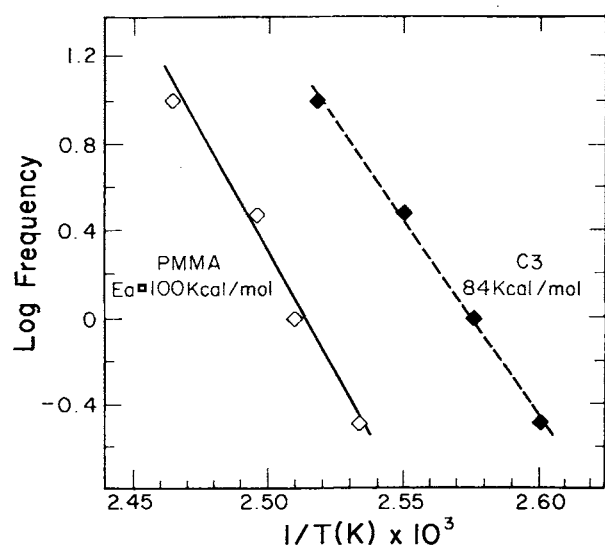


Figure 8 Arrhenius plot of relaxation maxima vs. frequency for PMMA and C3 graft copolymer.

The transition temperatures measured by DMTA compare well with the T_g measured by DSC, if frequency differences are taken into account (Tables II and III).

Since the T_g of the phase rich in graft chain appears around the same temperature as the β -relaxation of the PMMA, it is important to consider the shape and position of the peak. By comparing the peaks of PMMA, C3, and C6 curves around 20°C (Fig. 9), it is possible to observe a displacement of the maxima for the graft copolymers. The β -relaxation is not expected to be shifted by the presence of plasticizer.^{31,38} A blend of PMMA/Bu(EO)(PO)OH (60/40) prepared to test the displacement of the peak shows the maximum at -40°C (Fig. 8, Table IV). A very broad peak is observed for the β -relaxation of PMMA, while the C3 and C6 peaks remain sharp.

Table IV shows the physical blend composition influence on T_g 's. The presence of two T_g 's means that the physical blends are also partially immiscible. By comparing the results for C1 (12 wt % of graft chain) and C3 (18 wt % of graft chain) (Table III) and, respectively, PMMA/Bu(EO)(PO)OH (90/10) and PMMA/Bu(EO)(PO)OH (80/20) (Table IV), it is possible to observe that the two transitions of the blends are located at lower temperature than the two transitions of the graft copolymer. This behavior seems to be related to the entropic factor and the influence of the end group.

CONCLUSIONS

The pyrolysis of PMMA begins at $\sim 250^\circ\text{C}$ and for PEO-*b*-PPO and PMMA graft copolymers at \sim

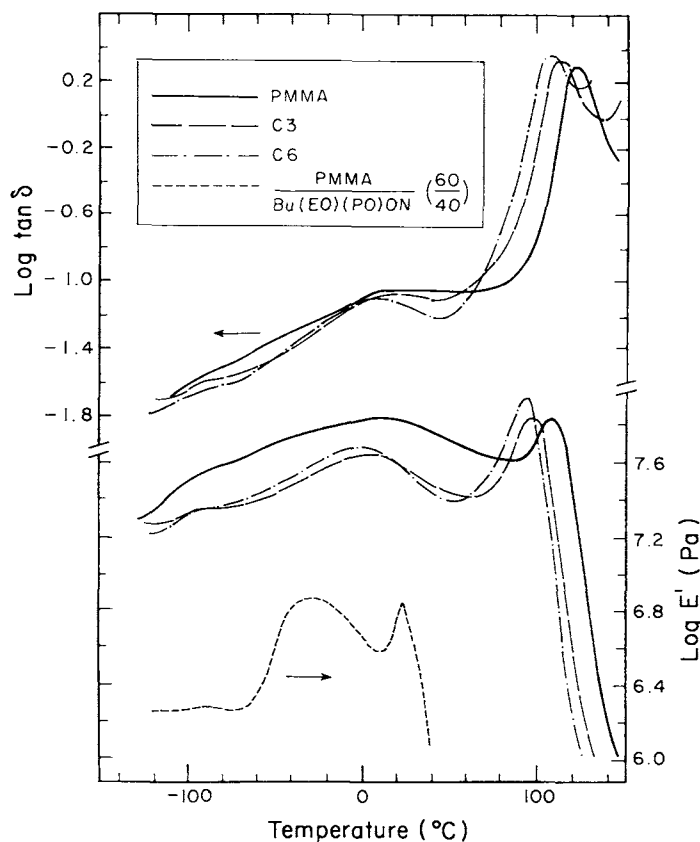


Figure 9 Thermal scan of loss E'' moduli and $\tan \delta$ at 1 Hz, for PMMA, C3, and C6 graft copolymer and PMMA/Bu(EO)(PO) (60/40) blend.

160°C. The graft copolymer TGA curves differ from that of the physical blend: for blends, the degradation process is characteristic of each polymer constituent; for graft copolymer, the pyrolysis begins on the graft chain with a reaction at the main and graft chain link being evident.

The graft copolymers are two phase (two T_g 's). The mutual miscibility depends on graft content and structure. The DSC and dynamic mechanical tran-

sitions show the same results (if frequency and heating rate differences are accounted): the graft copolymers are partially immiscible, and the physical blend of PMMA and PPO/PEO block copolymer were also immiscible. This despite that PMMA/PPO and PMMA/PEO physical blends have been reported to be miscible for the same compositions.^{1,2} The immiscibility is a function of graft content and it is also a function of graft structure: the Bu(PO)(EO) graft provides more miscibility in the graft copolymer than Bu(EO)(PO) grafts, as judged by shifts in T_g 's.

Data on physical blend [PMMA and Bu(CO)-(PO)OH] do show partial miscibility and the results differ from the corresponding graft copolymers. The two transitions of the blend (10°C and 77°C) are located at a lower temperature than the two transitions of the graft copolymer (23°C and 113.5°C) for the same composition (see dynamic data for sample C3 in Table III). This behavior seems to be related to: (1) the entropic factor differences of blends and graft copolymers, and (2) the influence of the end-group. For the graft copolymer, graft end

Table IV Dynamic Mechanical Measurements, Transition Temperatures of Physical Blends

Composition (wt %)		T_g (°C)	T_g (°C)
PMMA	Bu(EO)(PO)		
90	10	5	80
80	20	10	77
70	30	1	56
60	40	-25	38

$\tan \delta$, damping peak; 1 Hz; 2°C/min.

is a butyl group. For the blend, the Bu(EO)(PO)OH has two end groups, butyl group and hydroxyl group. The latter will interact with the ester group of PMMA.

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