Thermal Behavior of Random Copolymers of Methacrylic Acid and *tert*-Butyl Methacrylate

Juey H. Lai

Honeywell Corporate Technology Center, Bloomington, Minnesota 55420.
Received March 4, 1983

ABSTRACT: Thermal behavior of random copolymers of methacrylic acid (MAA) and *tert*-butyl methacrylate (TBM) and of homopolymers, poly(methacrylic acid) (PMAA) and poly(*tert*-butyl methacrylate) (PTBM), has been studied by infrared spectroscopy (IR), differential scanning calorimetry, and thermogravimetric analysis in the temperature range 25–300 °C. The results of this study suggest that at 200 °C anhydride bonds are formed in the copolymers and the predominant products of the reactions are terpolymers of MAA, TBM, and methacrylic anhydride (MAN). Similarly, the homopolymers PMAA and PTBM are mostly converted into copolymers of MAA and MAN and copolymers of TBM and MAN, respectively, at 200 °C, with a small fraction of polymers depolymerized. At 250 °C, however, the major reaction product for all copolymers and the homopolymers is poly(methacrylic anhydride). Thermally induced anhydride bonds, on the basis of IR studies, are mainly intramolecular in nature.

Introduction

Poly(methyl methacrylate) and other lower methacrylates depolymerize thermally to monomers when heated to a high temperature. Poly(methacrylic acid) (PMAA), when heated to a temperature higher than 200 °C, is thermally converted into poly(methacrylic anhydride) (PMAN) with a small fraction of the polymer depolymerized.[1] It has been speculated that poly(*tert*-butyl methacrylate) (PTBM), when heated to higher temperatures, is also converted into PMAN preceded by the formation of PMAA.[1] In this paper, we report the thermal behavior of the copolymers of TBM and MAA and of homopolymers PTBM and PMAA, in the temperature range 25–300 °C. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were employed. We have found that the copolymers and the two homopolymers are all converted into PMAN at 250 °C. Significant degradation of PMAN occurs at approximately 400 °C. Thermally induced anhydride bonds, on the basis of IR studies, are mainly intramolecular rather than intermolecular.

Experimental Section

The monomers, MAA and TBM, were obtained from Eastman Kodak Co. and Polysciences, Inc., respectively. The monomers were vacuum distilled before use. The polymerization of MAA/TBM copolymers was performed in chlorobenzene, using AIBN (2,2-azobisisobutyronitrile) as a free radical initiator. After polymerization, the precipitated copolymers were washed twice with petroleum ether and dried in a vacuum oven at 50 °C for 24 h. To obtain copolymers of different compositions and to control the uniformity of the composition, the monomer ratios and reaction times were varied in the polymerization. The polymerization conditions are shown in Table I.

Both homopolymers, PMAA and PTBM, were obtained from Polysciences, Inc. PMAA was used as received. PTBM was redissolved in a solvent, precipitated in a nonsolvent, and dried before use. The composition of MAA/TBM copolymers was determined by elemental analysis (carbon and hydrogen) performed by Galbraith Laboratories, Knoxville, TN. The information on the molecular weight and molecular weight distribution of the copolymers was obtained by using a Waters Associates Model 202 gel permeation chromatograph (GPC) with monodisperse polystyrene as the standard and tetrahydrofuran as the solvent. The characteristics of the copolymers are shown in Table II.

Thermal behavior of the polymers was studied by using a DuPont 990 differential scanning calorimeter, a DuPont 951 thermogravimetric analyzer,[2] and a Digilab 14C Fourier transform infrared spectrometer. For IR studies, the polymer films were coated on a KCl substrate and placed in a holder with a heating element and a thermocouple. IR spectra of absorbance vs. wavenumber were recorded as a function of temperature.

Results and Discussion

DSC thermograms for the MAA/TBM copolymer-B in the temperature range 25–300 °C are shown in Figure 1. The thermogram for the copolymer-B which was baked at 50 °C in air exhibits a broad endotherm with a peak at 230 °C. A similar thermogram but with a smaller endotherm was obtained for copolymer-B baked at 200 °C in air for 30 min before DSC runs. No endotherm was found for copolymer-B baked at 250 °C in air for 30 min. Instead a shift in the base line of the DSC trace was found to be occurring at 158 °C. Similar behavior was observed for the other copolymers, copolymer-A, copolymer-C, and copolymer-D, and the two homopolymers PTBM and PMAA.

The glass transition temperature of PMAN and PMAA are listed as 159 and 228 °C, respectively.[3] The results of DSC studied indicate that, irrespective of copolymer composition, TBM/MAA copolymers are converted into PMAN after baking at 250 °C. Similarily, both homopolymers, PTBM and PMAA, are also converted into PMAN after baking at 250 °C. The fact that DSC thermograms for the low-temperature (50 °C) baked sample show a broad endotherm suggests that anhydride bonds are continuously formed as the polymer is heated from room temperature to 300 °C.

Although baking the polymers at 200 °C does induce considerable numbers of anhydride bonding between neighboring side groups, it appears that all possible bondings are not completed by baking at 200 °C in air for 30 min. DSC thermograms taken for 200 °C baked polymers still exhibit the endotherm but the peak is smaller and less broad.

TGA thermograms for the homopolymers, PMAA and PTBM, and the MAA/TBM copolymers, copolymer-B, copolymer-C, and copolymer-D, are shown in Figure 2. The percent weight loss data for the polymers at 250 ° C obtained from TGA thermograms are shown in Table III. Theoretical weight loss due to complete formation of anhydride bonds between adjacent groups for PMAA and PTBM without depolymerization are also shown in Table III. Experimentally observed weight loss for PTBM at 250 °C is 44.0%, which is close to the theoretical value of 45.7%. This suggests that at 250 °C PTBM is nearly completely converted into poly(methacrylic anhydride) without significant depolymerization. Experimentally

0024-9297/84/2217-1010$01.50/0

Table I
Polymerization Conditions for MAA/TBM Copolymers

polymer	monomer vol, mL MAA	monomer vol, mL TBM	solvent vol, mL	AIBN wt., mg	polym temp, °C	polym time, h
copolymer-A	15	15	180	40	55	3
copolymer-B	12	18	180	40	55	4
copolymer-C	10	20	180	40	55	5
copolymer-D	8	22	180	40	55	5.5

Table II
Characteristics of MAA/TBM Copolymers

polymer	composition, mol % MAA	composition, mol % TBM	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
copolymer-A	80.3	19.7	507 000	359 000	1.41
copolymer-B	68.9	31.1	579 000	405 000	1.43
copolymer-C	64.7	35.3	640 000	469 000	1.36
copolymer-D	55.7	44.3	609 000	378 000	1.61

Table III
TGA Results for the Polymers

polymer	% weight loss at 250 °C exptl	% weight loss at 250 °C theor
PMAA	16.0	10.5
MAA/TBL copolymer-A	32.0	
MAA/TBM copolymer-B	34.0	
MAA/TBM copolymer-C	37.0	
MAA/TBM copolymer-D	39.0	
PTBM	44.0	45.7

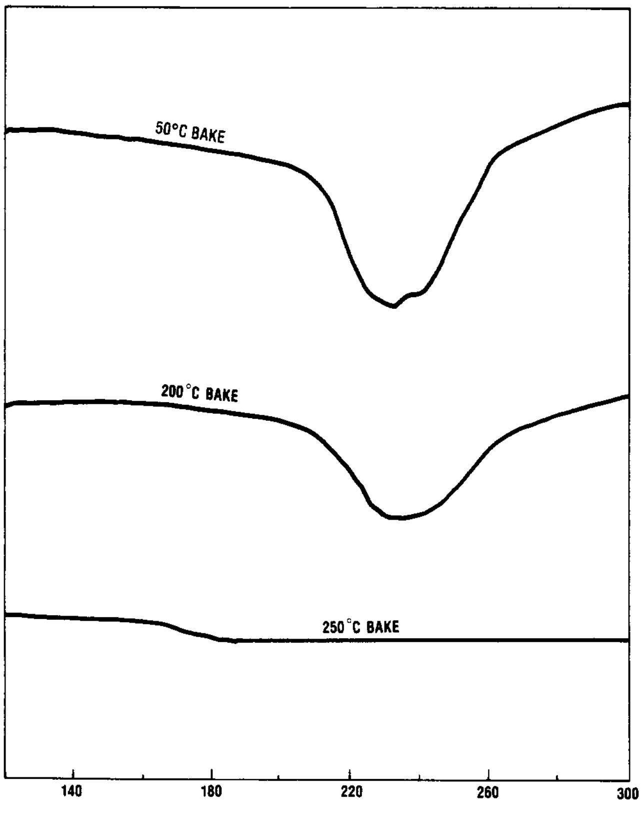

Figure 1. DSC thermograms for MAA/TBM copolymer-B. Heating rate was 10 °C/min.

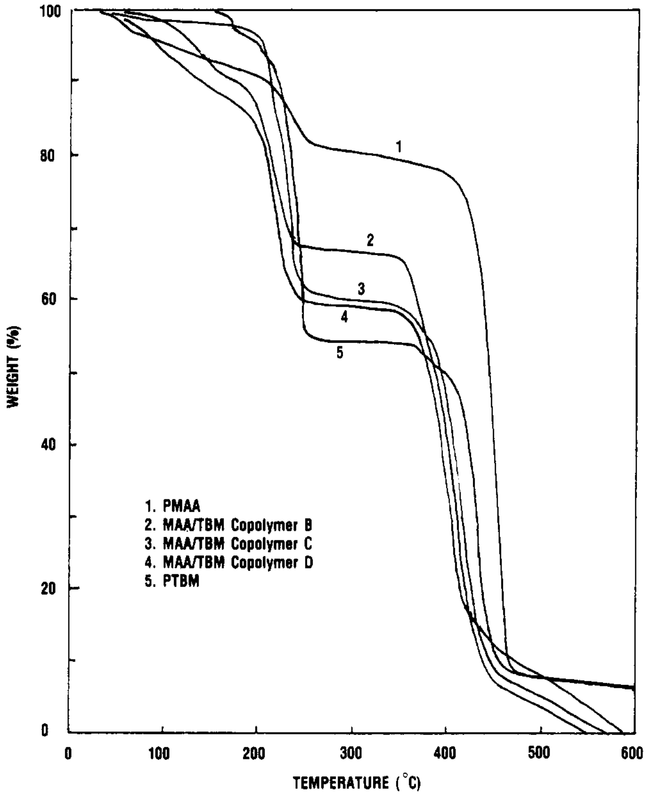

Figure 2. TGA thermograms for MAA/TBM copolymers, PMAA and PTBM. Heating rate was 10 °C/min.

observed weight loss for PMAA at 250 °C is 16.0%, which is somewhat higher than the theoretical value of 10.5%. The cause of larger weight loss is probably due to loss of solvent, loss of sorbed water, and the loss of monomer due to small degree of depolymerization.[1] As expected, percent weight loss for the copolymers at 250 °C increases with an increase in TBM content in the copolymers.

Of particular interest is whether intra- or intermolecular anhydride bonds are formed in the copolymers when they are heated. IR spectra which plot absorbance vs. wavenumber for the homopolymers PTBM and PMAA and copolymer-B are shown in Figures 3–5. The spectra for the three polymers show the following common characteristics: (1) the intensity of the broad OH absorption in the range 2500–3600 cm^{-1} decreases with an increase in temperature, (2) the presence of intense C–O–C (anhydride) peak at 1022 cm^{-1} appears at 200 °C, and its intensity of absorption increases with an increase in temperature, (3) disappearance of the carboxylic acid carbonyl peak at 1700 cm^{-1} begins at 200 °C; at the same time, the anhydride carbonyl twin peaks at 1750 and 1800 cm^{-1} begin to appear. The lower frequency absorption is more intense. Similar behavior has been observed in the IR spectra of the other MAA/TBM copolymers.

According to Grant and Grassie,[1] the six-membered glutaric anhydride type ring formed between adjacent carboxyl groups (intramolecular) has double peaks at 1756 and 1802 cm^{-1}, with the lower frequency absorption being more intense. The intermolecular isobutyric anhydride ring formed between acid groups attached to different chains has double peaks at 1743 and 1803 cm^{-1}, but with the higher frequency absorption being more intense.

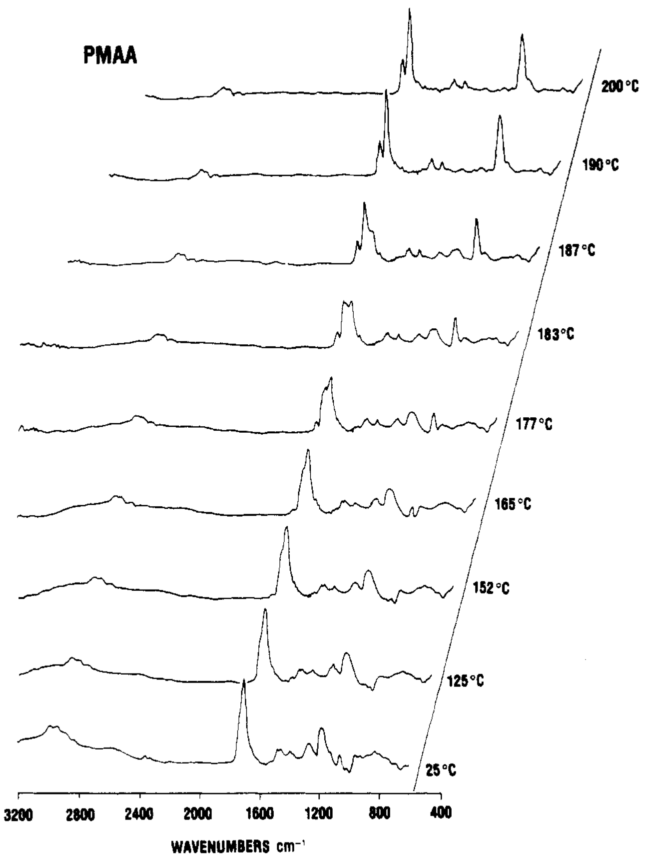

Figure 3. IR spectra of PMAA as a function of temperature.

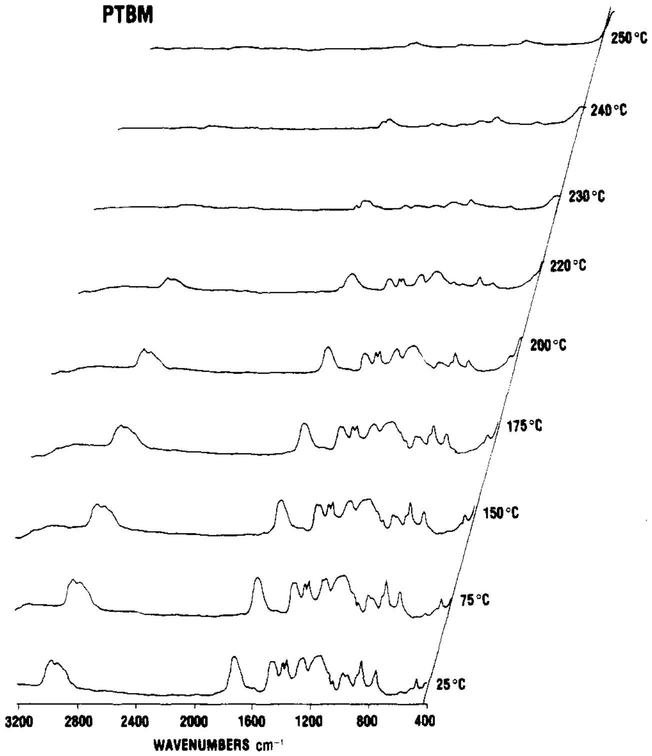

Figure 4. IR spectra of PTBM as a function of temperature.

Thermal treatment of PTBM has been studied by Matsuzaki et al.[4] They found that the isotactic PTBM polymerized with Grignard reagent lost weight at 180–200 °C, resulting in anhydride formation. For the syndiotactic PTBM polymerized with γ-rays, the polymer undergoes two-step reaction, deesterification, and subsequent anhydride formation.

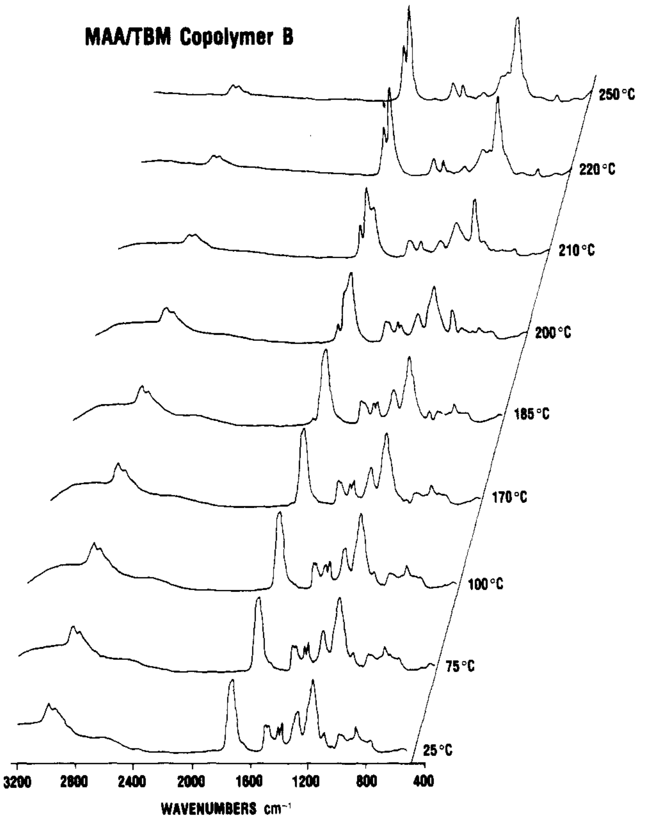

Figure 5. IR spectra of MAA/TBM copolymer-B as a function of temperature.

A kinetic study of anhydride formation in isotactic and atactic PMAA has been performed at 200 °C by Geuskens et al.[5] They have found that the reactions obey first-order kinetics and the reaction rate (i.e., rate of water loss) is about 4 times higher for the isotactic PMAA than for the atactic polymer. The arrangement of neighboring carboxyl groups was found to be more favorable for the formation of a cyclic anhydride by intramolecular reaction in isotactic PMAA.

The results of this study thus indicate that at 250 °C all polymers, MAA/TBM copolymers, and PMAA and PTBM homopolymers are mostly converted into PMAN, with the majority of the anhydride bonds being intramolecular rather than intermolecular anhydrides. At 200 °C, MAA/TBM copolymers are mostly converted into MAA/TBM/MAN terpolymers, while PMAA and PTBM are mostly converted into MAA/MAN copolymers and TBM/MAN copolymers, respectively. It is possible that long baking at 200 °C could possibly convert polymers further into PMAN. However, such experiments have not been conducted in our study.

Acknowledgment. Part of this work was supported by the U.S. Army Electronics Technology and Devices Laboratory (ERADCOM), Fort Monmouth, NJ. The author wishes to thank B. Fure, L. Hallgren, and R. Douglas for their technical assistance.

References and Notes

(1) D. H. Grant and N. Grassie, *Polymer*, 1, 135 (1960).
(2) P. F. Levy, *Am. Lab. (Fairfield, Conn.)*, Jan 1970, 46–58.
(3) J. Brandrup and E. H. Immergut, Eds., "Polymer Handbook", Wiley-Interscience, New York, 1975.
(4) K. Matsuzaki, T. Okamoto, A. Ishida, and H. Sobue, *J. Polym. Sci., Part A*, 2, 1105 (1964).
(5) G. Geuskens, E. Hellinckx, and C. David, *Eur. Polym. J.*, 7, 561 (1971).