Investigation of Thermal Behavior of Poly(2-hydroxyethyl methacrylate-*co*-itaconic acid) Networks

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ABSTRACT: The thermal behavior of poly(2-hydroxyethyl methacrylate) [PHEMA] homopolymer and poly(2-hydroxyethyl methacrylate-*co*-itaconic acid) [P(HEMA/IA)] copolymeric networks synthesized using a radiation-induced polymerization technique was investigated by differential scanning calorimetry, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The glass-transition temperature (T_g) of the PHEMA homopolymer was found to be 87°C. On the other hand, the T_g of the P(HEMA/IA) networks increased from 88°C to 117°C with an increasing amount of IA in the network system. The thermal degradation reaction mechanism of the P(HEMA/IA) networks was determined to be different from the PHEMA homopolymer, as confirmed by thermogravimetric analysis. It was observed that the initial thermal degradation temperature of these copolymeric networks increased from 271°C to 300°C with IA content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1602–1607, 2007

Key words: hydrogels; synthesis; thermal properties

INTRODUCTION

Polymethacrylates degrade to lower-molecular-weight compounds or to monomers by heating or irradiation with high-energy radiation. A mechanism involving random homolytic scission of the chain followed by a series of intermolecular and intramolecular transfer reactions and with considerable formation of monomer has been suggested.[1,2] The degradation or stability of polymethacylates relates to their structures, such as type of ester group, molecular weight and distribution, stereoregularity, and copolymer composition. For polymethacrylates having a side chain with a higher functional group, such as —OH, the chemical structure of the polymer changes via intra- and inter-chain reaction of side groups, which results in cross-linking, cyclization, and so on.[3,4] Poly(2-hydroxyethyl methacrylate) (PHEMA) is the most widely studied member of this group.[5–9]

The most widely used biomedical hydrogel is water-swollen, crosslinked PHEMA. The PHEMA structure permits a water content similar to that of living tissue. The hydrogel is inert to normal biological processes, shows resistance to degradation, is permeable to metabolites, is not absorbed by the body, withstands heat sterilization without damage, and can be prepared in a variety of shapes and forms. The polymer glass-transition temperature, T_g, representing the molecular mobility of the polymer chains is an important phenomenon that influences the material properties and potential applications of a given polymer.

A few studies on thermal degradation of PHEMA have been reported in the literature.[1,5–7,9] PHEMA has a hydroxyl group (—OH). However, itaconic acid (IA) has two carboxylic acid groups (—COOH), and it may be able to form intramolecular six-membered cylic anhydrides at around 250°C–300°C. It is interesting to study to what extent the P(HEMA/IA) copolymers exists and how the thermal degradation of PHEMA is affected by incorporating IA segments in the copolymer.

In this study, we examined the effects of composition on the thermal behavior of P(HEMA/IA) copolymers using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR).
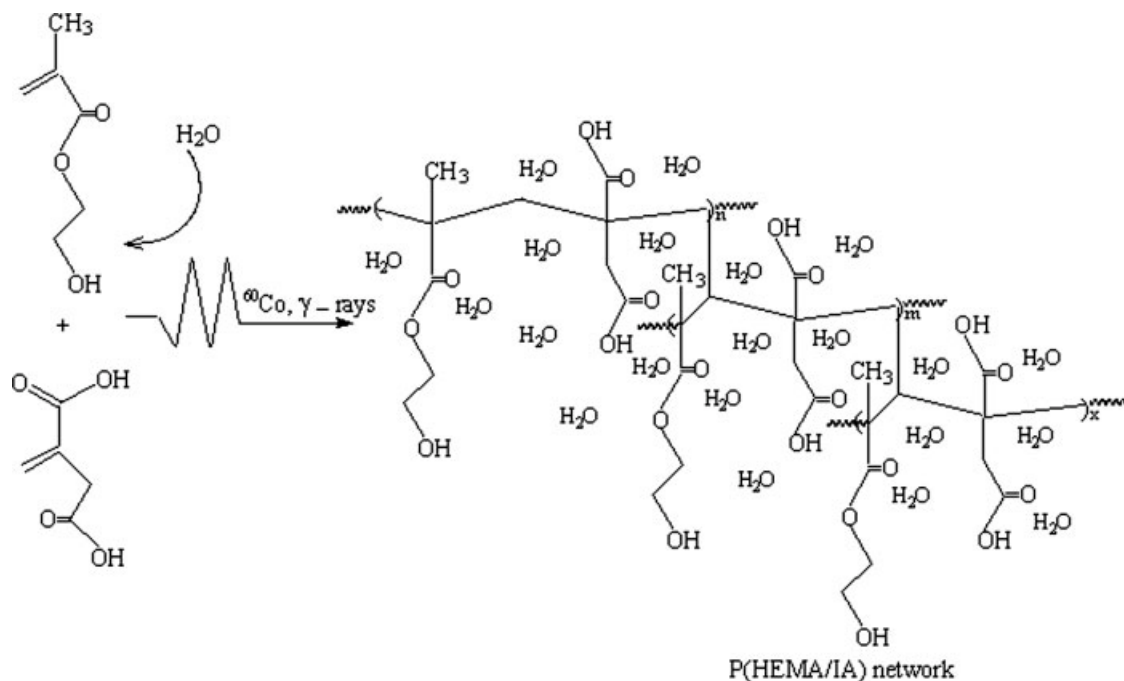
EXPERIMENTAL

Preparation of copolymers

The two monomers used in this study, HEMA and IA, were obtained from Merck (Darmstadt, Germany) and BDH (Poole, UK), respectively. The P(HEMA/IA)

Scheme 1

copolymers were prepared by the radiation-induced simultaneous processes of polymerization and self-bridging of HEMA and IA in aqueous solutions without the use of any crosslinker by the following procedure (see Scheme 1). Aqueous solutions of monomers were prepared in 1.0 mL of pure water in different compositions (HEMA/IA mole ratios of 97.3 : 2.7, 96.0 : 4.0, 94.7 : 5.3, 92.1 : 7.9 and 88.9 : 10.1). The prepared monomer solutions were placed in 4-mm-diameter PVC straws and irradiated at 2.8 kGy in air at ambient temperature in a PX-γ-30 Isslodovateji irradiator at a fixed dose rate of 3.36 kGy/h. Copolymers obtained in long cylindrical shapes were cut into pieces 3–4 mm long. The pieces were dried in a vacuum oven at 315 K to a constant weight and subjected to Soxhlet extraction with water, which removed the uncrosslinked polymer and the unreacted IA. The extracted network pieces were dried again in a vacuum oven at 42°C to a constant weight. The amount of unreacted IA in the aqueous extract was determined by titration with NaOH (0.05M) to a phenolphthalein end point, but no titrate was consumed for all P(HEMA/IA) copolymers reaching 100% conversion, which was obtained for all mixtures after 2.8 kGy irradiation.

To completely remove water, the copolymers obtained were maintained at 120°C for 3 h under nitrogen flux before characterization by DSC, TGA, and FTIR.

Differential scanning calorimetry

The glass-transition temperatures of the pure PHEMA and P(HEMA/IA) copolymeric networks were deter-

mined with a TA Instruments DSC 2010 thermal analyzer system (Delaware, USA). The DSC was calibrated with metallic indium (99.9% purity). All polymers were tested in crimped aluminum pans at a heating rate of 10°C/min under dry N_2 gas (25 mL/min) over a temperature range from 10°C to 200°C. The glass-transition temperatures were determined as the average of at least three separate measurements as the midpoints of reverse-S-shaped thermograms. The experimental error in the individual measurements was estimated to be less than 0.5°C.

Thermogravimetric analysis

The dynamic weight loss tests were conducted on a TA Instruments 2050 thermogravimetric analyzer (TGA). All tests were conducted in a N_2 purge (25 mL/min) using sample weights of 5–10 mg over a temperature range of 20°C–600°C at a scan rate of 10°C/min.

Fourier transform infrared spectroscopy

FTIR spectra of original and thermally degraded polymers were measured on a Nicolet 520 FTIR spectrophotometer. The samples were prepared by making KBr (potassium bromide) pellets containing 3 wt % of the materials.

RESULTS AND DISCUSSION

DSC

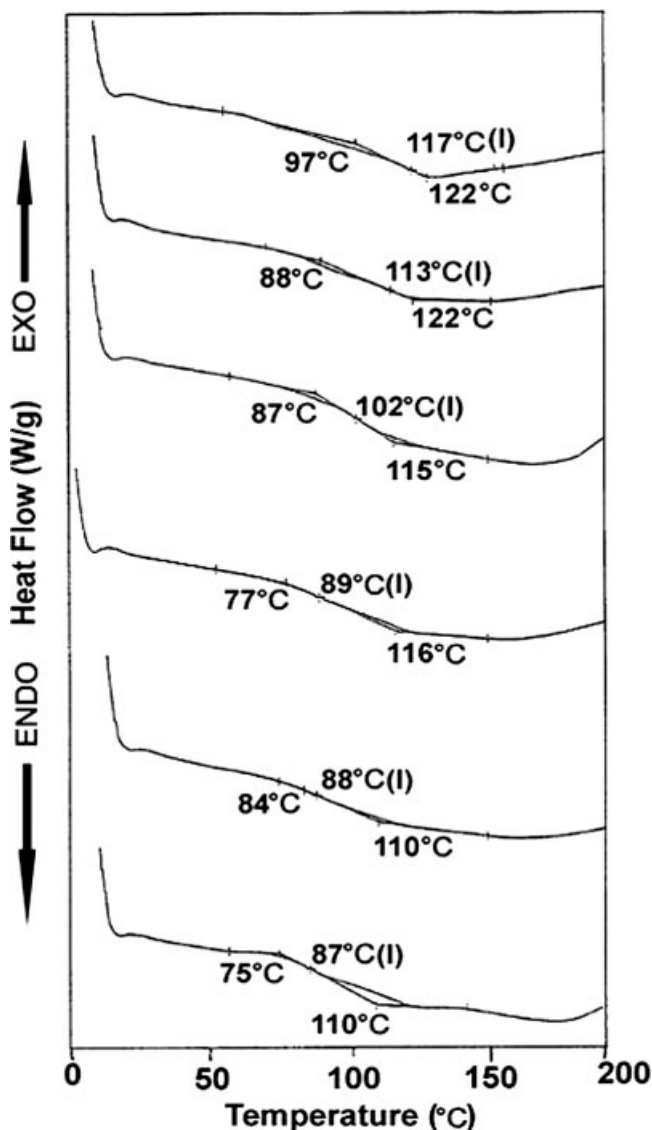DSC sensitively detected the small heat capacity change because of the glass transition for PHEMA and

Figure 1 DSC thermograms of P(HEMA/IA) networks containing various mole percentages of IA: (a) 10.1%, (b) 7.9%, (c) 5.3%, (d) 4.0%, (e) 2.7% (f) PHEMA.

the P(HEMA/IA) networks (Fig. 1). The observed glass-transition temperatures (T_g) are depicted by arrows in Figure 1. It is well known that PIA has very low thermal stability. The T_g of PIA cannot be measured because degradation commences first, accompanied by broad endothermic peaks in the DSC thermogram. However, PHEMA is a thermally more stable polymer. Its T_g value is 87°C and degradation starts at approximately 322°C. Several conflicting T_g values for PHEMA have been reported in the literature, with T_gs ranging from 85°C to 105°C.[10–12] This behavior may be attributed to the large influence of the bound water because of the hygroscopic nature of the PHEMA. It is well known that the homopolymers or copolymers of HEMA always contain about 10 wt % water, even after several months of drying

at 50°C temperature under vacuum. The T_g depression is consistent with the plasticization theory.[13] For all copolymer networks and PHEMA homopolymer, a single T_g value was clearly observed, and each observed T_g depended on the copolymer composition. This suggests that the copolymers have a random copolymer structure for all compositions. On the other hand, it can be seen that the T_g was low for the PHEMA homopolymer ($T_g = 87$°C) compared with that of the PHEM/IA copolymers. However, the T_g for the P(HEMA/IA) networks increased from 88°C to 117°C with the increase in the IA content of the copolymer. This behavior may be attributed to the crosslinker effect of IA.[14] In addition, it could also be responsible for the interactions between the hydroxyl and the carboxylic acid groups increasing depending on the IA content in the P(HEMA/IA) copolymer.

TGA

To examine the effect of composition on the thermal degradation of the P(HEMA/IA) copolymeric networks, we measured TG curves for all the samples from 20°C to 600°C. Typical weight loss (TG) and derivative of weight loss (DTG) curves of PHEMA and P(HEMA/IA) copolymers at a heating rate 10°C/min under a nitrogen atmosphere are shown in Figures 2 and 3. From the TG curves, the initial degradation and final degradation temperatures were determined. From the DTG curves, the maximum temperature of weight loss was also noted.

The mass loss of PHEMA began at about 322°C and reached its maximum at 361°C. The TG curve of PHEMA homopolymer indicated one reaction stage [Fig. 2(f)], which was reflected as a single peak in the DTG curve [Fig. 3(f)]. The initial degradation temperature of PHEMA showed that the degradation to be a result of random chain scission.[9] On the other hand, the P(HEMA/IA) copolymers were a little low in thermal stability compared to that of the PHEMA homopolymer (Fig. 2). However, the initial degradation temperatures of P(HEMA/IA) networks increased slightly from 271°C to 300°C with increasing IA content. As can be seen in Figure 3(a–e), the P(HEMA/IA) networks degraded in two steps, as shown by the distinct peaks in the DTG thermograms. Two distinct reaction peaks, at around 365°C and 435°C, were identified in the DTG thermograms of P(HEMA/IA) networks. These peaks were attributed to ester formation and thermal degradation, respectively. This behavior showed that the thermal degradation reaction mechanism of the P(HEMA/IA) networks was an additional difference with the PHEMA homopolymer. This observation also indicated that this change may have corresponded to the formation of esters from the carboxylic acid groups
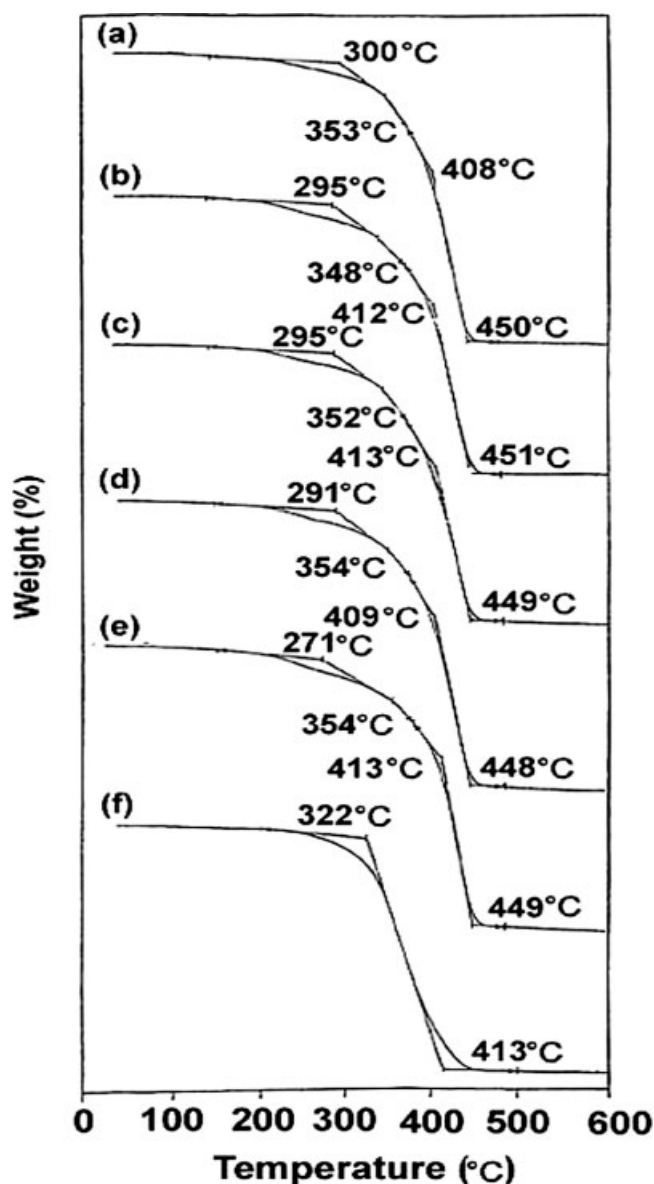
Figure 2 TG thermograms of P(HEMA/IA) networks containing various mole percentages of IA: (a) 10.1%, (b) 7.9%, (c) 5.3%, (d) 4.0%, (e) 2.7% (f) PHEMA.

and the hydroxyl groups in the P(HEMA/IA) copolymeric networks. However, there are several types of esters that could possibly be formed in these copolymeric networks. One of them is intermolecular ester, which is formed between the hydroxyl group of HEMA units and the carboxylic acid group of IA units, and the other is intramolecular ester, which is involved in the formation of six-member rings by the reaction of adjacent carboxylic acid groups of IA units (see Scheme 2). Similar types of these structures have previously been observed in the degradation products of other polymer systems.[15] The initial step in the degradation of poly(methacrylic acid) is the formation of cyclic six-membered ester groups from the acid functionalities. At high temperatures it

also undergoes massive degradation to yield a highly aromatic structure with phenolic groups. The thermal analysis results of poly(methacrylic acid) and poly(acrylic acid) studied by Fyfe and McKinnon[15] were also similar to the data reported here, with the formation of six-membered rings the predominant process observed.

FTIR

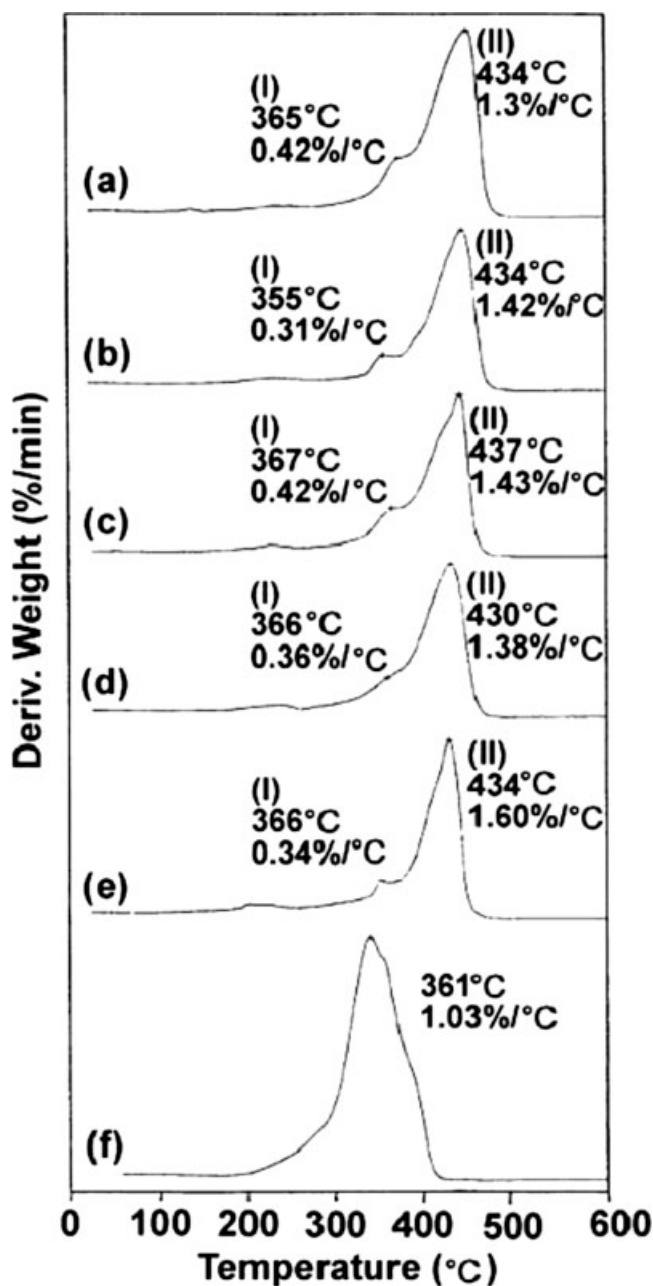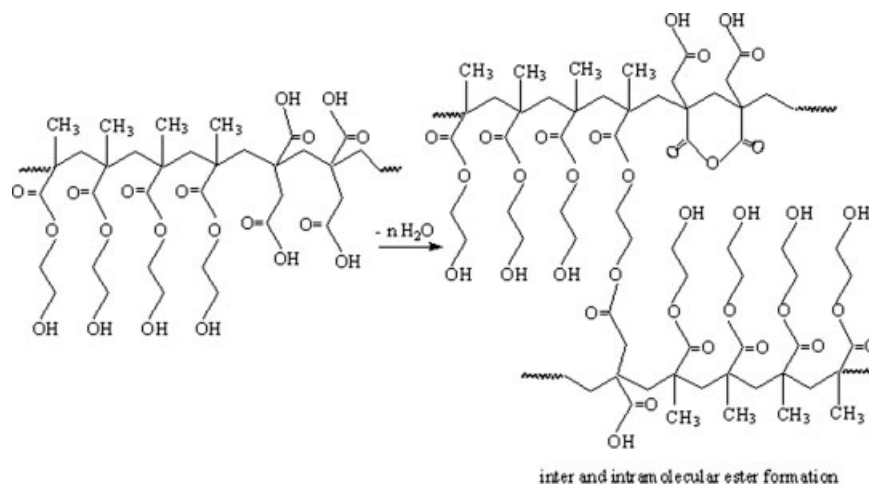In thermal degradation studies, P(HEMA/IA)-3 networks were partially degraded under an N_2 flow at

Figure 3 DTG thermograms of P(HEMA/IA) networks containing various mole percentages of IA: (a) 10.1%, (b) 7.9%, (c) 5.3%, (d) 4.0%, (e) 2.7% (f) PHEMA.

inter and intramolecular ester formation

Scheme 2

a heating rate of 10°C/min 250°C, 300°C, and 450°C. The FTIR spectra of the char yields were recorded at each heating stage (Fig. 4). As shown in Figure 4, the spectrum of the P(HEMA/IA) heated to 250°C was the same as that of the original copolymeric network, but at 300°C some changes were observed, such as a relative decrease in the intensity of the broad O—H band at about 3450 cm^{-1} and the appearance of a shoulder at 1640 cm^{-1} (C=C), labeled on the spectrum, and a band at 2250 cm^{-1} (CO$_2$). In this case, a shoulder at 1640 cm^{-1} shows depolymerization to monomer. Many polymethacrylate esters easily give their monomers in thermal degradation, if they do not bear a strained ring or an easily breaking group in their side chain.[9] In addition to depolymerization, ester formation becomes more important with increasing temperature. The decrease in intensity of the O—H band could be obtained from the ratio of the integrated intensities of the O—H band at around 3450 cm^{-1} and the C=O bands around 1700 cm^{-1}. The ratio of the integrated OH/C=O band was 0.81 in the original P(HEMA/IA) network, whereas for the P(HEMA/IA) heated to 300°C it was 0.68. As a result, the data indicated that the overall degradation process at 300°C consisted of two reactions as the major reactions: depolymerization to monomer and ester formation.

CONCLUSIONS

In this study, the effect of copolymer composition on the thermal behavior of P(HEMA/IA) copolymers was investigated. The T_g of P(HEMA/IA) copolymers increased from 88°C to 117°C with an increase in IA content. On the other hand, the initial degradation temperatures of these copolymers also increased slightly, from 271°C to 300°C with increasing IA content of the copolymer. This behavior was attributed to the crosslinker effect of IA. Two distinct reaction
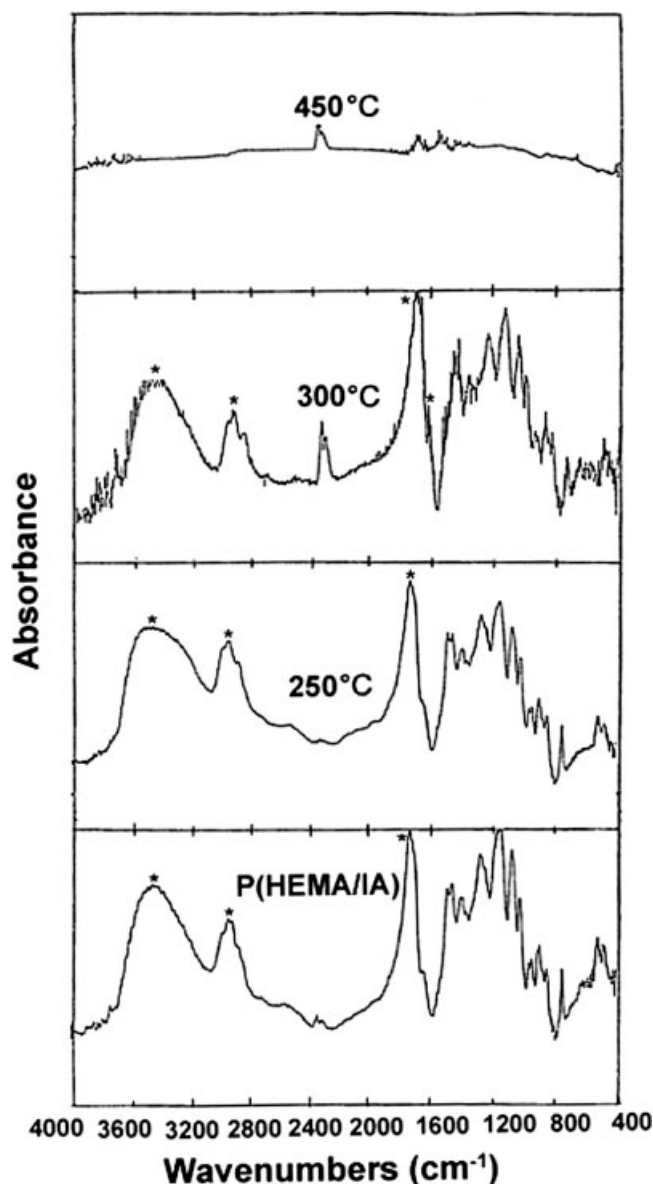

Figure 4 FTIR spectra of the partially degraded P(HEMA/IA) network containing 10.1% of IA.

peaks, at around 365°C and 435°C, were identified in the DTG thermograms of the P(HEMA/IA) networks. These peaks were attributed to ester formation and thermal degradation.

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