

Bulk Polymerization and Characterization of Isocyanatoacrylate Copolymers

MARTIN D. POWER,¹ CECIL C. CHAPPELOW,¹ CHARLES S. PINZINO,¹ J. DAVID EICK²

¹ Midwest Research Institute, Kansas City, Missouri 64110-2299

² School of Dentistry, Department of Oral Biology, University of Missouri–Kansas City, 650 East 25th Street, Kansas City, Missouri 64108-2795

Received 10 November 1997; accepted 6 January 1998

ABSTRACT: The purpose of this investigation was to prepare by bulk polymerization six new isocyanatoacrylate copolymers and to characterize them. The isocyanatoacrylate copolymers, which were prepared by tri-*n*-butylborane oxide (TBBO)-initiated free-radical polymerization, were formed from 1 : 1 mol mixtures of 2-isocyanatoethyl methacrylate (IEM) with 2-hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), 2-hydroxyethyl thiomethacrylate (HETMA), ethylthioethyl methacrylate (ETEMA), 2-(acetoxycetoxy)ethyl methacrylate (AAEMA), and tetrahydrofurfuryl methacrylate (THFMA). These six copolymers were compared to the homopolymer of IEM, which was polymerized in an identical fashion. The bulk polymers were fractionated into their acetone-soluble and acetone-insoluble components. Physical characterization via photoacoustic infrared (PASIR) spectroscopy showed vast differences in residual isocyanate content. Differential scanning calorimetry (DSC) thermal analysis was carried out on all polymers. Elemental analysis (nitrogen) determined the ratio of IEM to the comonomer and boron analysis showed whether the initiator stayed in the acetone-insoluble fraction or was “extracted” into the acetone-soluble fraction. In conclusion, we found that the composition of the copolymers correlated well with the predicted design. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1577–1583, 1999

Key words: bulk polymerization; isocyanatoacrylate; copolymers; free radical polymerization; differential scanning calorimetry; tri-*n*-butyl borane oxide (TBBO)

INTRODUCTION

Isocyanatoacrylates are attractive as bioadhesives because they are bifunctional. The polarized double bond can polymerize in the same fashion as do other acrylates and methacrylates, forming

a strong polymer with a carbon backbone. The isocyanate can function as an electrophile, reacting with groups such as hydroxy, amino, or other nucleophilic moieties. This bifunctionality can thereby increase adhesion to substrates or crosslinking to comonomers.^{1–7}

The goal of this study was to examine the free-radical polymerization of 2-isocyanatoethylethyl methacrylate (IEM) with six comonomer methacrylates and to characterize the resulting polymers by thermal analysis, elemental analysis, and FTIR. It was predicted that the resulting polymers would have residual isocyanate groups for

This study was supported in part by a grant from the National Institute of Dental Research, NIH.

Correspondence to: J. David Eick.

Contract grant sponsor: National Institute of Dental Research, NIH; contract grant number: DE09696.

Journal of Applied Polymer Science, Vol. 74, 1577–1583 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/061577-07

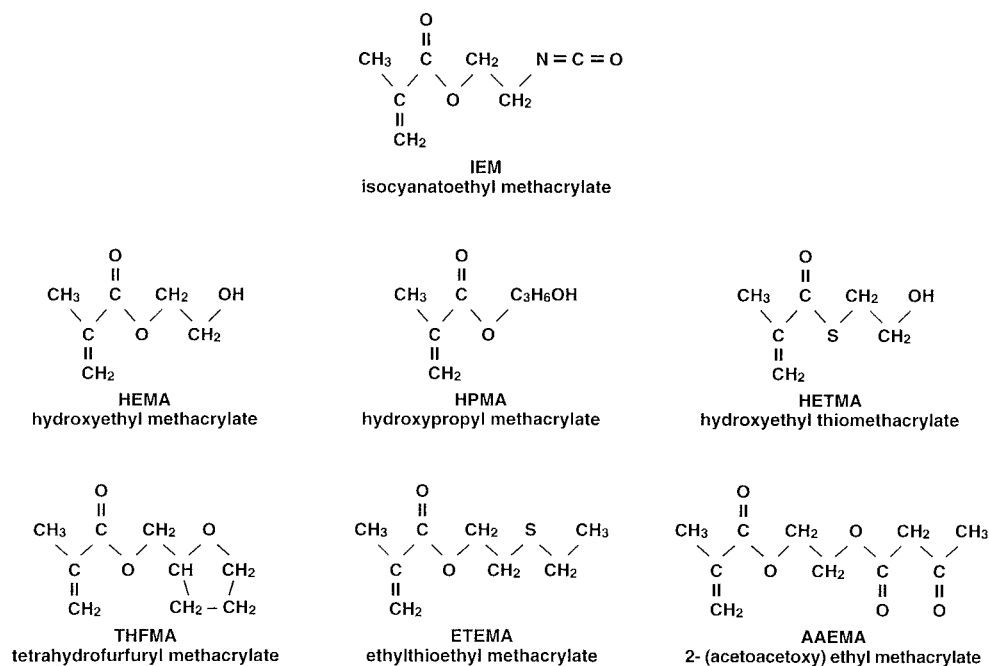


Figure 1 Structures of methacrylate monomers.

covalent bonding with hydroxyl or amino groups of the substrates. Hence, 2-isocyanatoethyl methacrylate was polymerized in bulk on a 3-g scale by itself and as a 1 : 1 mixture with six different comonomers. These comonomers were 2-hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), 2-hydroxyethyl thiomethacrylate (HETMA), ethylthioethyl methacrylate (ETEMA), 2-(acetoxyacetoxy)ethyl methacrylate (AAEMA), and tetrahydrofurfuryl methacrylate (THFMA) (Fig. 1). The polymerizations were carried out using tri-*n*-butyl borane oxide as the free-radical initiator. The temperature of each polymerization was recorded as a function of time. The resulting polymers were fractionated into their acetone-soluble and -insoluble components and analyzed physicochemically.

EXPERIMENTAL

Materials

Except for HETMA, which was prepared at the Midwest Research Institute and characterized by GC and GC/MS, all methacrylates used in this study were procured from commercial sources (IEM and ETEMA: Monomer-Polymer & Dajac Laboratories, Inc., Treviso, PA; HEMA, HPMA,

THFMA, and AAEMA: Aldrich, Milwaukee, WI). All commercially procured methacrylates were vacuum-distilled prior to use to remove the inhibitors except for ETEMA, which was passed through an inhibitor-removing column prior to use. The free-radical initiator TBBO was prepared at the Midwest Research Institute by the controlled oxidation of tri-*n*-butylborane (TBB, Callary Chemical Co., Evans City, PA) using a variation of the procedure described by Nakabayashi et al.⁸ Anhydrous acetone was procured from a commercial source and stored over 3 Å molecular sieves prior to use.

Methods

All bulk polymerizations were carried out with a total of 3 g of monomer, with the comonomers in a 1 : 1 mol ratio. Each polymerization was carried out in a 16 × 60-mm (7 mL) Nalgene tube with a round bottom. Reaction exotherms were measured using a J-type thermocouple (Fe—CuNi) attached to a digital thermometer. The thermocouple probe was placed in a melting point tube and submersed in the comonomer mixtures so that the tip of the thermocouple was in the middle of the tube and at half the height of the comonomer mixture (Fig. 2). Approximately 0.3 g of the TBBO initiator was added and the comonomer

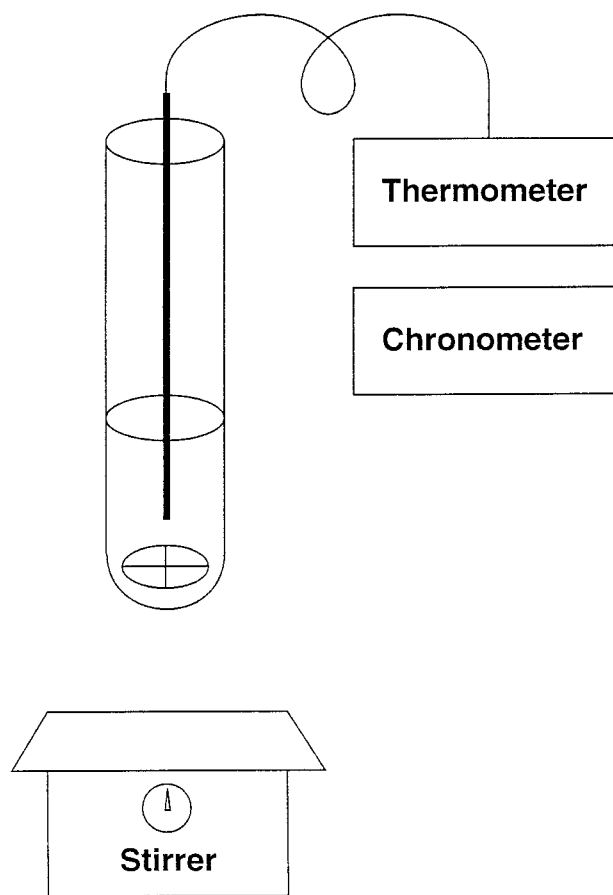


Figure 2 Bulk polymerization apparatus.

mixture was stirred at first with the glass-lined thermocouple and then with a magnetic stir bar using an external magnetic stir plate. Time = 0 s is defined as the addition of the catalyst TBBO. The temperature was recorded at 15-s intervals for a period of 60 min. At time = 60 min, the hard samples were broken out of the Nalgene tubes and placed in 30 mL of anhydrous acetone. The resulting mixture was heated to reflux for 30 min and allowed to cool to room temperature. The solids were collected by gravity filtration and dried for 3 h in a vacuum oven at 60°C. The filtrate was concentrated on a rotary evaporator and dried for 3 h in a vacuum oven at 60°C. The 14 resulting fractions were analyzed by differential scanning calorimetry (DSC), FTIR or photoacoustic infrared (PASIR), and elemental analysis (carbon, hydrogen, and nitrogen; Galbraith Laboratories, Inc.). The DSC was run using a DuPont Model 1090 thermal analyzer with a DuPont Model 910 differential scanning calorimeter

(20–25 mg samples, 5-min equilibration, nitrogen flow of 40 mL/min). The liquid samples were characterized by FTIR (Perkin–Elmer 283) spectroscopy and the solid samples were characterized by PASIR (Analect RFX-75A Rapid-Scan Interferometer, Laser Precision Corp., using an MTEC photoacoustic detector Model 200, MTEC Photoacoustics, Inc.) spectroscopy. The seven acetone-insoluble fractions were also analyzed by boron elemental analysis.

DATA AND RESULTS

IEM Homopolymer

To IEM (3.056 g, 19.70 mmol), TBBO (0.221 g) was added to yield a white solid. The maximum polymerization temperature was 63°C at 915 s. Fractionation yielded 3.389 g of acetone-insoluble material and 0.20 g of acetone-soluble material. The total recovered was 110% by mass.

Elemental analysis: Found 54.72% C; 6.67% H; 8.37% N. Theoretical: 54.19% C; 5.85% H; 9.03% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed an exotherm of 2.30 J/g at 105.6°C and an exotherm of 148 J/g at 301.8°C (Fig. 3). FTIR was consistent with the predicted spectrum (Fig. 4), showing a large isocyanate absorption at 2250 cm^{-1} , C—H stretching vibrations at 2900–3000 cm^{-1} , and carbonyl absorptions at 1700 cm^{-1} .

IEM/HEMA Polymer

To a mixture of IEM (1.631 g, 10.51 mmol) and HEMA (1.372 g, 10.52 mmol), TBBO (0.291 g) was added to yield a white solid. The maximum polymerization temperature was 162°C at 720 s. Fractionation yielded 3.230 g of acetone-insoluble material and 0.34 g of acetone-soluble material. Total recovered was 108% by mass.

Elemental analysis: Found: 52.56% C; 7.17% H; 4.01% N. Theoretical: 54.73% C; 6.71% H; 4.91% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed what appears to be an inflection point at 190.0°C which may correspond to a glass transition temperature (Fig. 5). The FTIR spectra of the IEM homopolymer and the IEM/HEMA copolymer were similar with the exception that the isocyanate band was absent in the copolymer (Fig. 6).

IEM/ETEMA Polymer

To a mixture of IEM (1.422 g, 9.165 mmol) and ETAMA (1.600 g, 9.182 mmol), TBBO (0.286 g)

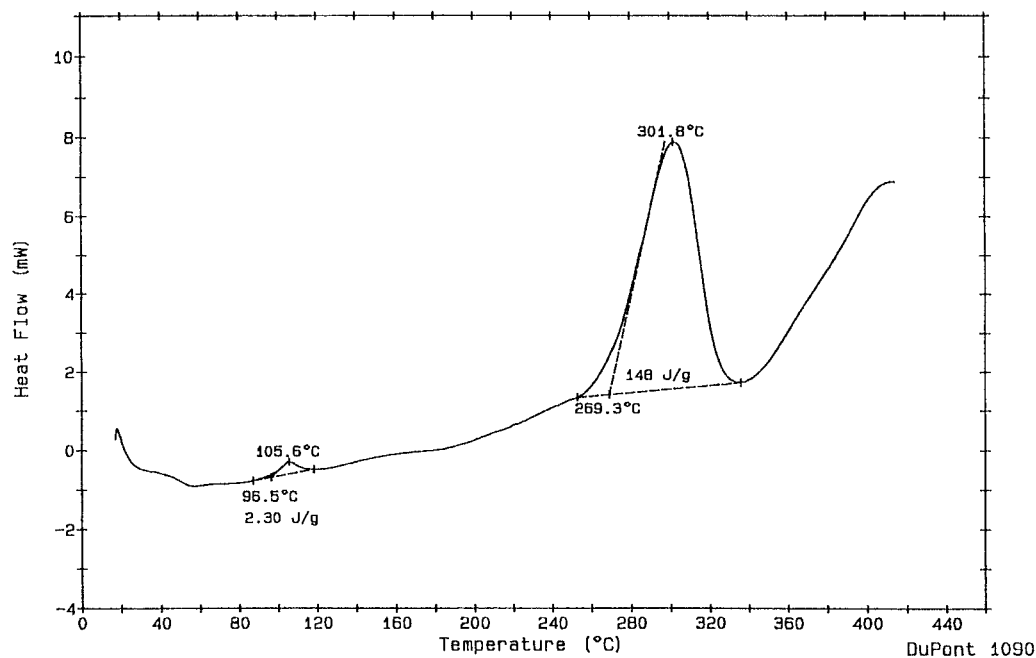


Figure 3 DSC trace of IEM polymer-acetone-insoluble fraction.

was added to yield a white solid material. The maximum polymerization temperature was 32°C at 45 s. Fractionation yielded 3.244 g of acetone-insoluble material and 0.44 g of acetone-soluble material. Total recovered was 111% by mass.

Elemental analysis: Found: 55.02% C; 7.87% H; 4.00% N. Theoretical: 54.69% C; 7.04% H; 4.68% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed an endotherm of 38.9 J/g at 273°C and a second endotherm of 199.9 J/g at 358°C. FTIR was similar to the FTIR of the IEM polymer.

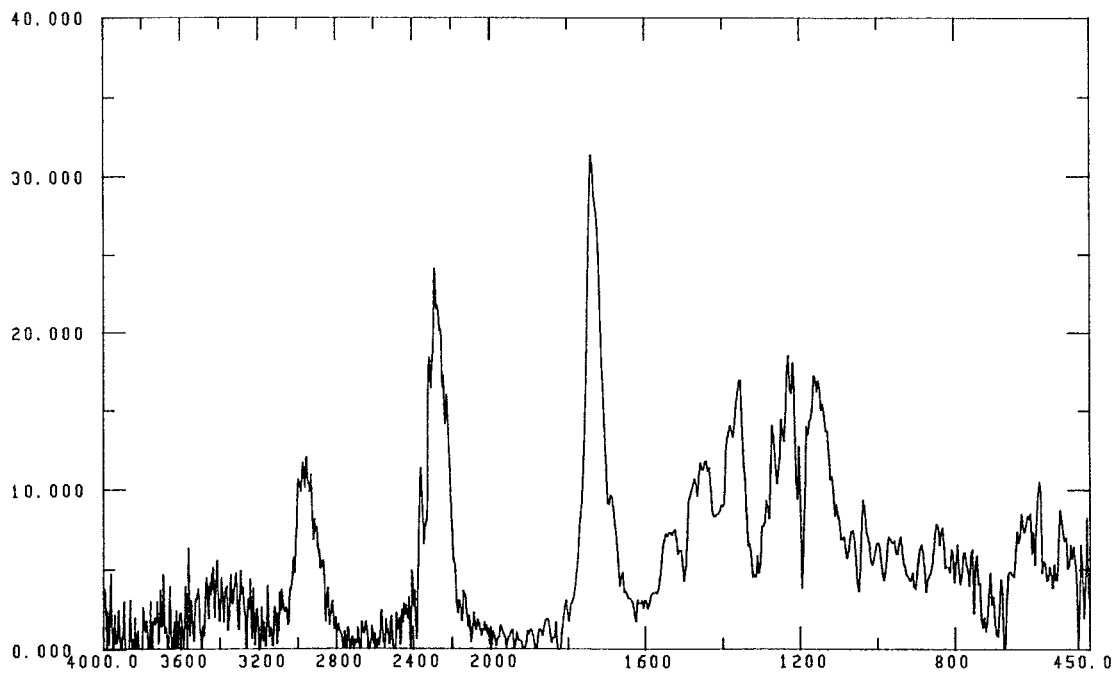


Figure 4 FTIR of IEM polymer-acetone-insoluble fraction.

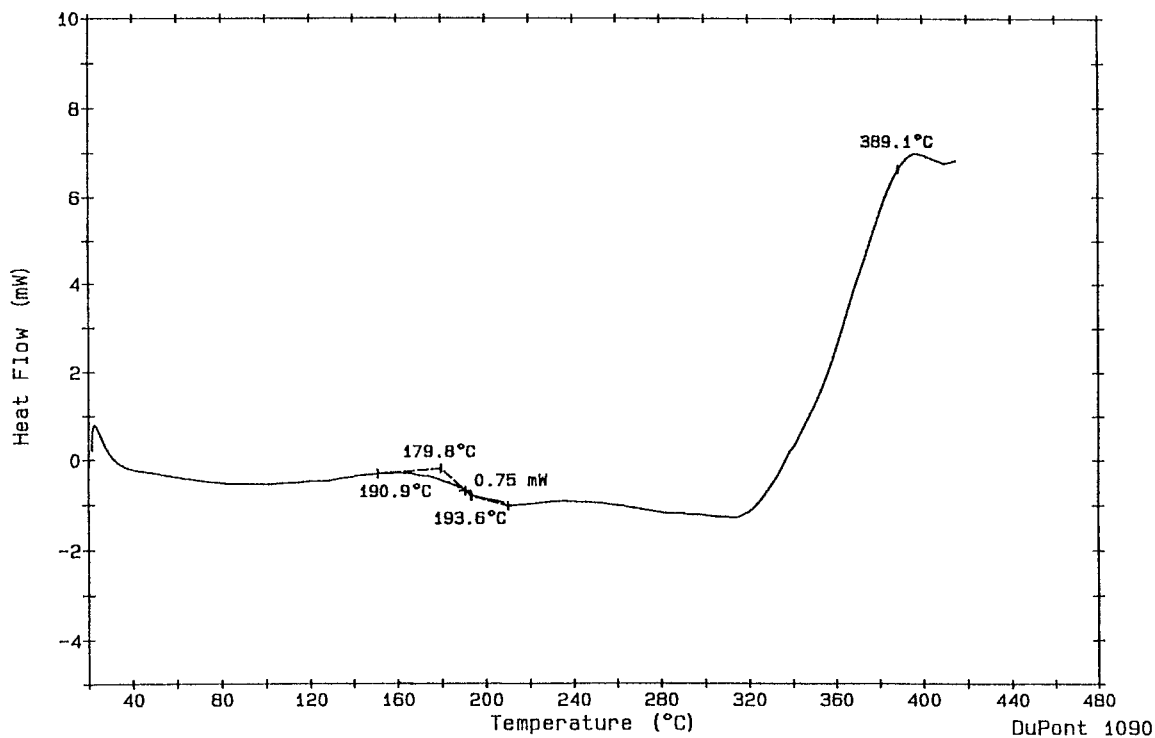


Figure 5 DSC trace of IEM/HEMA polymer-acetone-insoluble fraction.

IEM/HPMA Polymer

To a mixture of IEM (1.547 g, 9.971 mmol) and HPMA (1.442 g, 10.00 mmol), TBBO (0.286 g) was

added to yield a white solid. The maximum polymerization temperature was 39°C at 45 s. Fractionation yielded 3.11 g of acetone-insoluble ma-

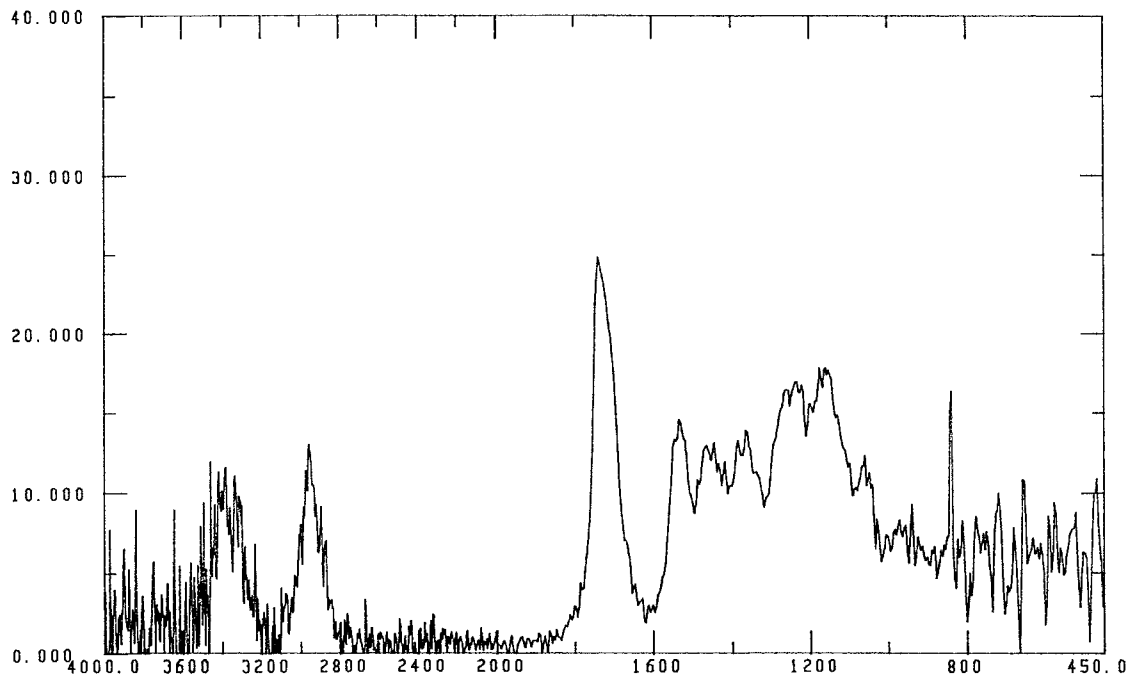


Figure 6 FTIR of IEM/HEMA polymer-acetone insoluble fraction.

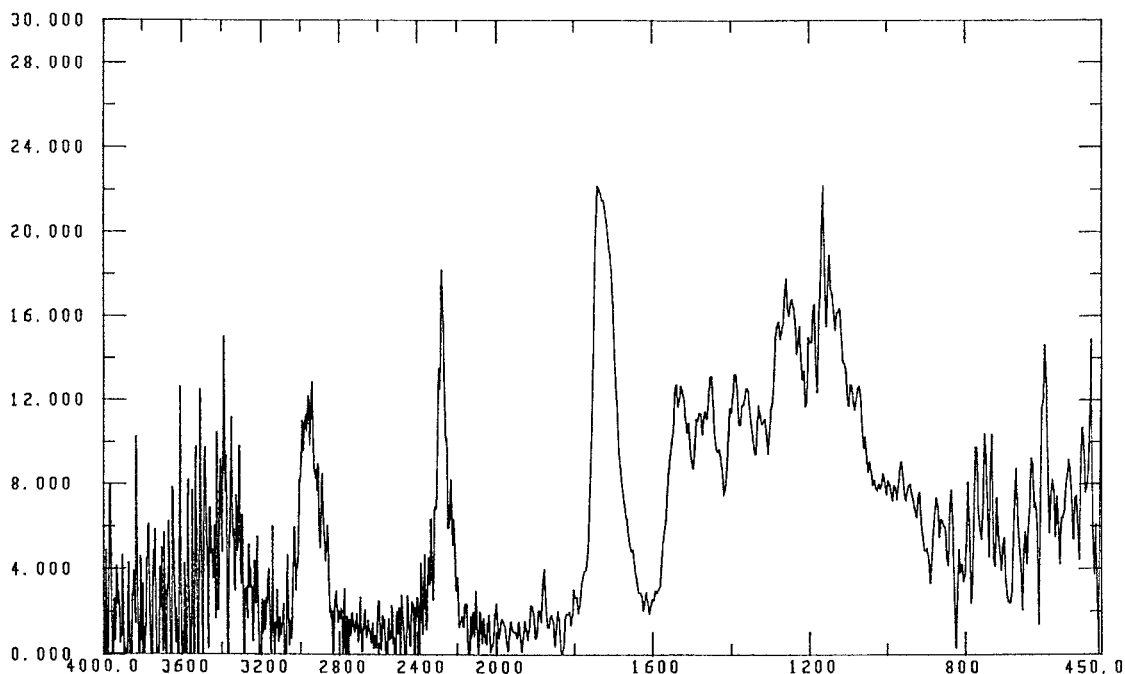


Figure 7 FTIR of IEM/HPMA polymer-acetone-insoluble fraction.

terial and 0.54 g of acetone-soluble material. Total recovered was 112% by mass.

Elemental analysis: Found: 55.44% C; 7.88% H; 4.16% N. Theoretical: 56.18% C; 7.07% H; 4.68% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed an inflection point at approximately 187°C and a baseline shift beginning at 340°C. FTIR was similar to the IEM polymer IR (Fig. 7).

IEM/AAEMA Polymer

To a mixture of IEM (1.277 g, 8.231 mmol) and AAEMA (1.741 g, 8.13 mmol), TBBO (0.296 g) was added to yield a white rubbery solid. The maximum polymerization temperature was 55°C at 510 s. Fractionation yielded 3.277 g of acetone-insoluble material and 0.38 g of acetone-soluble material. Total recovered was 110% by mass.

Elemental analysis: Found: 56.08% C; 7.47% H; 3.42% N. Theoretical: 55.28% C; 6.28% H; 3.79% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed a baseline shift beginning at 340°C, presumably due to decomposition. FTIR was similar to the IEM polymer spectrum except for a larger carbonyl band.

IEM/THFMA Polymer

To a mixture of IEM (1.430 g, 9.217 mmol) and THFMA (1.566 g, 9.200 mmol), TBBO (0.297 g)

was added to yield a white solid material. The maximum polymerization temperature was 79°C at 1050 s. Fractionation yielded 3.175 g of acetone-insoluble material and 0.46 g of acetone-soluble material. Total recovered was 110% by mass.

Elemental analysis: Found: 52.89% C; 6.45% H; 8.14% N. Theoretical: 59.07% C; 7.13% H; 4.30% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed a sinusoidal baseline that could not be interpreted. FTIR was similar to the IEM polymer spectrum.

IEM/HETMA Polymer

To IEM (1.543 g, 9.945 mmol) and HETMA (1.460 g, 9.986 mmol), TBBO (0.299 g) was added to yield a white solid material. The maximum polymerization temperature was 30°C at 195 s. Fractionation yielded 2.554 g of acetone-insoluble material and 0.97 g of acetone-soluble material. Total recovered was 107% by mass.

Elemental analysis: Found: 51.89% C; 7.08% H; 4.30% N. Theoretical: 51.81% C; 6.35% H; 4.65% N.

Thermal (DSC) analysis of the acetone-insoluble fraction showed an endotherm of 132.0 J/g at 302°C. FTIR was similar to the IEM polymer spectrum.

DISCUSSION

The highest largest maximum polymerization temperature was in the IEM/HEMA sample. This is most likely due to the crosslinking reaction of HEMA's primary alcohol with the isocyanate of IEM. Although this is normally only observed in the presence of tin(II) salts or tertiary amines, both the heat of polymerization and the presence of small amounts of TBB (a Lewis acid) can promote this addition reaction. The absence of an isocyanate band in the FTIR of the IEM/HEMA polymer supports this rationale. Oxygen is very important to the progress of the reaction. This was demonstrated in a separate experiment in which the IEM/HEMA polymerization was attempted in an inert (nitrogen gas) atmosphere. No reaction exotherm was observed. After the nitrogen atmosphere was replaced with an air atmosphere, the reaction occurred as before.

All the polymers were crystalline in appearance and possessed a white-to-off-white color. Interestingly, the IEM-AAEMA polymer turned to a two-colored polymer of white and yellow. The two-colored solids were manually separated from one another. It was predicted that all the polymers would have residual isocyanate groups. All the PASIR analyses of the acetone-insoluble fractions showed a residual isocyanatoacrylate functionality in the region of 2200–2300 cm^{-1} with the exception of the IEM/HEMA. The acetone-soluble fractions agreed with the acetone-insoluble fractions.

With respect to the DSC exotherms at elevated temperatures, the symmetrical peak around 300°C for (Fig. 3) is attributed to polymerization of residual monomer and oligomers. Furthermore, the final temperature elevations starting at 340°C in the IEM homopolymer (Fig. 3) and

320°C in the IEM-HEMA polymer (Fig. 5) are most likely due to thermal decomposition of the samples.

CONCLUSIONS

1. The IEM and the IEM/comonomer mixtures can be polymerized by the addition of approximately 10 wt % TBBO in the presence of air.
2. The comonomer mixture with both the highest exotherm and the shortest-time-to-maximum exotherm is the IEM/HEMA mixture.
3. The IEM/HEMA polymer is highly cross-linked as observed by the absence of an isocyanate band in the FTIR.

REFERENCES

1. Mukai, N.; Ige, H.; Makino, T.; Atarashi, J. Eur. Patent Appl. EP 301 516 A2 890 201 (1989).
2. Brauer, G. M.; Lee, C. H. U.S. Patent Appl. US195 000 AO 890 215 (1989).
3. Brauer, G. M.; Lee, C. H. *J Biomed Mater Res* 1989, 23, 753–763.
4. Lee, C. H.; Brauer, G. M. *J Dental Res* 1989, 68, 484–488.
5. Brauer, G. M.; Lee, C. H. *Polym Mater Sci Eng* 1988, 59, 397–401.
6. Engelbrecht, J. Ger. Offen. DE 3634 354 A1 880 421 (1988).
7. Brauer, G. M.; Termimi, D. J.; Jackson, J. A. In *Durability of Macromolecular Materials*; ACS Symposium Series 95; American Chemical Society: Washington, DC, 1979; pp 393–410.
8. Nakabayashi, N.; Masuhara, E.; Machida, E.; Ohmori, I. *J Biomed Mater Res* 1978, 12, 149–165.