Grafting of β-Cyclodextrin-Modified 2-Hydroxyethyl Methacrylate onto Polyurethane

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SYNOPSIS

2-Hydroxyethyl methacrylate (HEMA) and β-cyclodextrin are bridged using toluene-2,4-diisocyanate (TDI) by reacting the —OH group of HEMA and one of the primary —OH groups of β-cyclodextrin. The modified HEMA is grafted to polyurethane by γ-irradiation. The preliminary study showed that the membrane potential of conventional polymers like polyurethane could be enhanced considerably by this type of modification. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Cyclodextrins are well known for their ability to form inclusion complexes with a variety of components.[1-4] Their ability particularly in distinguishing isomers has been well exploited in chromatography.[5]

The separation potential of conventional polymeric membranes in terms of specificity and selectivity could be enhanced severalfold by incorporating cyclodextrins (CDs) on to the backbone of the polymers. Indeed, efforts leading in this direction have been reported. Lee[6] prepared cellulose membranes containing CDs and investigated their preevaporation characteristics. Recently, Yamasaki and Mizoguchi[7] blended β-CD with poly(vinyl alcohol) and studied the selectivity of the resultant material. The main drawback of blended membranes, as reported by Hirai et al.[8] is the possibility of CD dissolution into the feed liquids. To overcome this, grafting of CD directly to the polymers would be advantageous. To allow such grafting, however, CD has to be modified. Attaching vinyl monomers to CD appears to be an interesting possibility, particularly considering the fact that vinyl monomers can easily be grafted to conventional polymers. This communication addresses the synthesis of a β-CD/2-hydroxyethyl methacrylate (HEMA) adduct and its subsequent grafting to polyurethane (PU).

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EXPERIMENTAL

2-Hydroxyethyl methacrylate (HEMA) and β-cyclodextrin (β-CD) were obtained from Sigma Chemicals, USA, and toluene-2,4-diisocynate (TDI) was obtained from Fluka, AGC, Germany. These chemicals were used without further purification. All other reagents (HPLC grade) were obtained from E. Merck, India.

Infrared (IR) spectra were recorded using a Perkin-Elmer Model 597 IR spectrophotometer. For obtaining the surface features, an ATR accessory (Perkin-Elmer) and KRS-5 crystal were employed along with the spectrophotometer.

A Waters Associates chromatographic system consisting of a Model 6000A solvent delivery pump, Model U6K injector, and Model 486 tunable absorbance detector was used for the chromatographic analysis. A μ-Styragel column (nominal pore size 10^3 Å) was used in conjunction with dimethylacetamide at a flow rate of 1 mL/min for estimating the molecular weight. The column effluents were monitored at 280 nm and the chromatograms were obtained on an Omini Scribe strip chart recorder (Houston Instruments, TX). The column was calibrated using polystyrene molecular weight standards. For other chromatographic analysis, an μ-Bondapak C_{18} column was used. The mobile phase was a water : methanol mixture (65 : 35 v/v) at a flow rate of 1 mL/min. The detection wavelength was 270 nm.

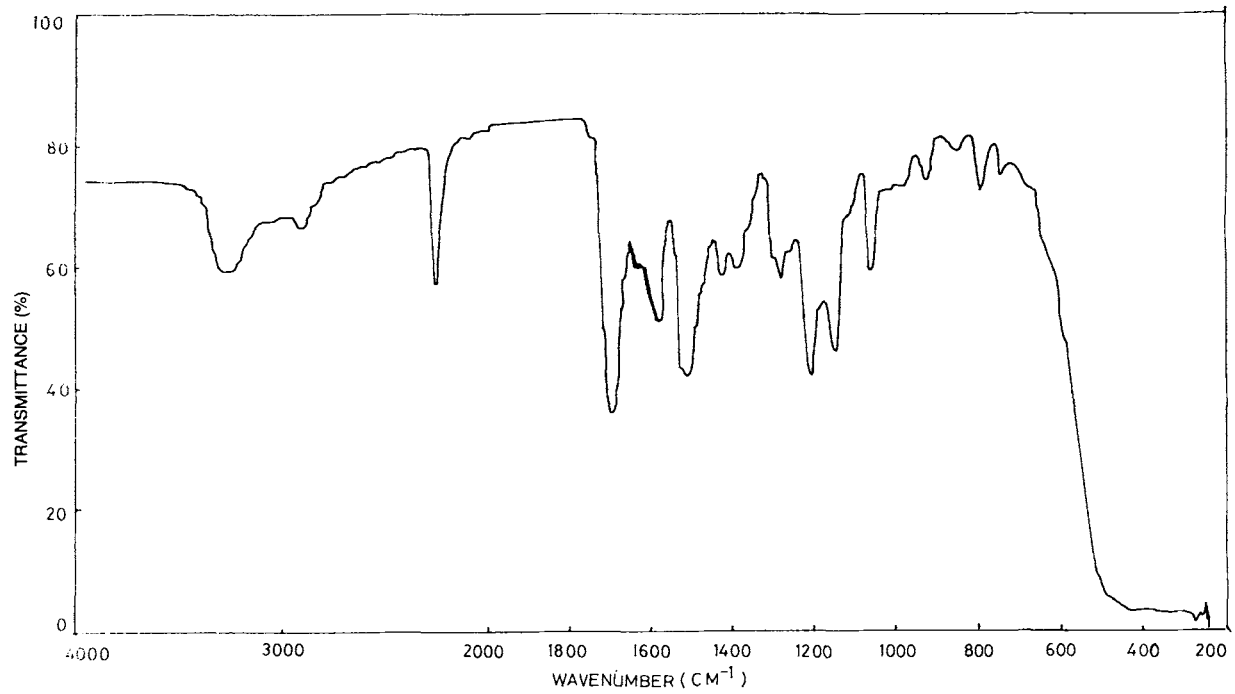

Figure 1 IR spectrum of the product formed between TDI–HEMA.

A Hitachi Model S-2400 scanning electron microscope was used for observing the surface of the polymers. A thin layer of gold was coated prior to observation.

For measuring the mechanical properties of the polymers, a Model 1193 universal testing machine (Instron, UK) was used. The testing was carried out as per ASTM D 882. The crosshead speed was 100 mm/min.

SYNTHESIS

The molar concentration was chosen in such a way to react only one —OH group of β-CD. We presumed equal probability to all the primary —OH groups of β-CD. The stoichiometry in this case was 0.5*M* HEMA : 1*M* TDI and 0.5*M* βCD.

TDI and HEMA (without removing the stabilizer) were mixed in 20 mL dimethylacetamide (DMAC); then, 0.1% dibutyltin dilaurate (catalyst) was added and stirred magnetically at room temperature (30°C) under a blanket of nitrogen. The stirring was continued for about 1 h. The solution, at this stage, was subjected to infrared spectroscopic analysis. A few drops of the solution were placed on a sodium chloride window and the DMAC was removed by blowing a stream of nitrogen across the cell. The sample was then scanned from 4000 to 600 cm^{-1}.

A calculated amount of β-CD was then added to this solution; next, 5 mL DMAC was added and then the solution was stirred for nearly 2 h. This solution was then subjected to IR analysis as mentioned before.

PU was used as a substrate for grafting the modified β-CD. The PU was based on methylene bis-(*p*-cyclohexyl isocyanate), 1,4-butanediol, and poly(tetramethylene glycol) (molecular weight 1000). The polymer having a hard-segment content of 45% (by weight) was synthesized as reported elsewhere.[9] PU strips having a thickness of 1 mm and 6 cm length and 2 cm width were placed in the modified β-CD solutions for swelling. The swelled strips were taken out, blotted with filter paper, and immediately subjected to γ-irradiation from a Co^{60} batch irradiator to a total dose of 0.5 Mrad. The polymer strips were washed with methanol and water and then vacuum-dried.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum of the product formed between TDI and HEMA. The peak corresponding to the —OH group of HEMA has nearly disappeared. The simultaneous presence of a peak around 3300 cm^{-1} shows the formation of a —NH group between —OH and —NCO groups. The prominent feature of the spectrum is the presence

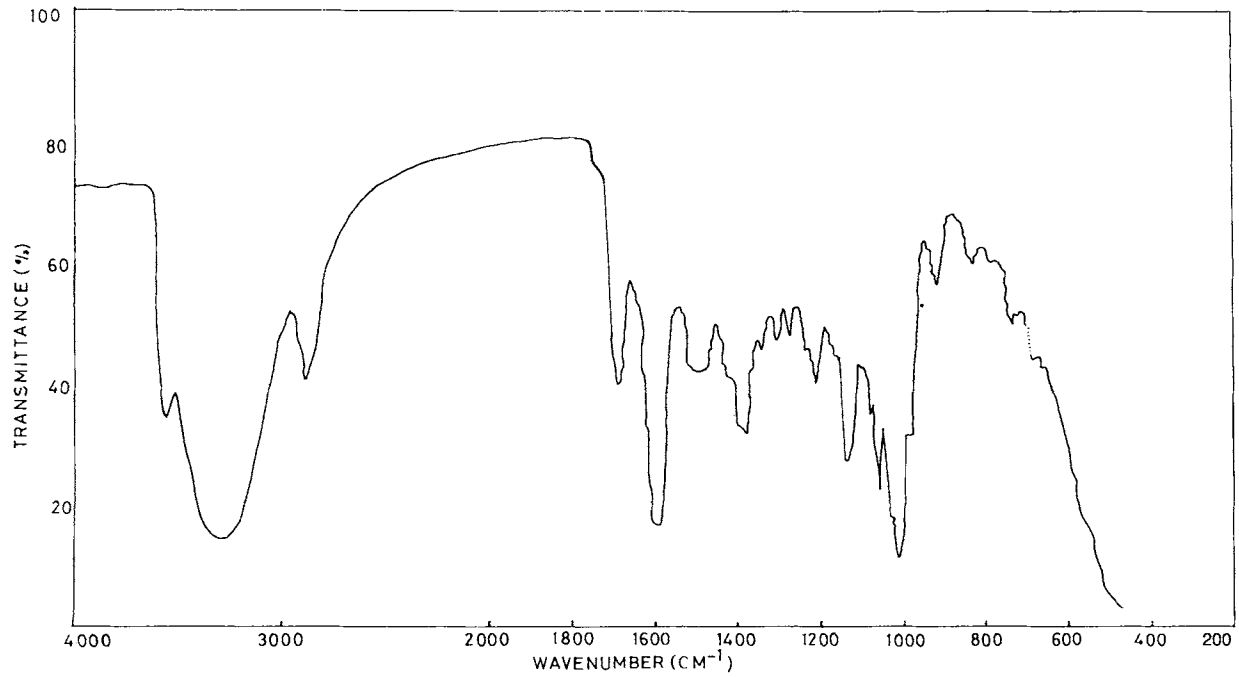

Figure 2 IR spectrum of the product formed between TDI–HEMA and β-CD.

of a peak centered around 2200 cm^{-1} characteristic of the —NCO group. The presence of this peak shows the availability of unreacted —NCO groups. A shoulder at 1640 cm^{-1} could be assigned to the double bond of HEMA and this, in fact, indicates that the double bond is intact.

Figure 2 depicts the spectrum of the component formed between HEMA–TDI and β-CD. The major differences between Figures 1 and 2 are the presence of a strong peak around 3500 and 1100 cm^{-1} together with the complete disappearance of 2200 cm^{-1} peak of —NCO. This suggests that the unreacted —NCO groups are reacted with the β-CD. The strong peaks centered around 3500 and 1100 cm^{-1} can be assigned to the —OH group and the acetal-type linkage of β-CD, respectively. The spectrum is consistent with the formation of HEMA–TDI–β-CD.

Figure 3 illustrates the gel permeation chromatographic trace of the product. The curve is homogeneous and the peak is relatively sharp, reflecting the formation of only a single entity. The molecular weight calculated from the curve is 1520, which is close to the theoretical value estimated from the molecular weight of β-CD (1135), HEMA (130), and TDI (174). The molecular weight obtained further supports the formation of the modified HEMA, namely, HEMA–TDI–β-CD.

Figure 4 shows the ATR–IR spectrum of the PU film grafted with the modified HEMA. The spectrum is nearly identical to the spectrum depicted in Figure 2, suggesting the grafting of the modified monomer onto the PU surface.

Figure 5(A) and (B) show the SEM micrographs of PU and modified PU. Figure 5(B) shows a distinctively altered surface, reflecting the grafting process.

The mechanical properties of the modified and unmodified PU are shown in Table I. The ultimate stress–strain parameters are reduced to some extent, indicating the grafting process. The extent of reduction, however, is not substantial, reflecting that the grafting has not taken place deep in the bulk of the polymer. It has generally been agreed that the ultimate mechanical properties of PU are governed by strain-induced soft-segment crystallization and

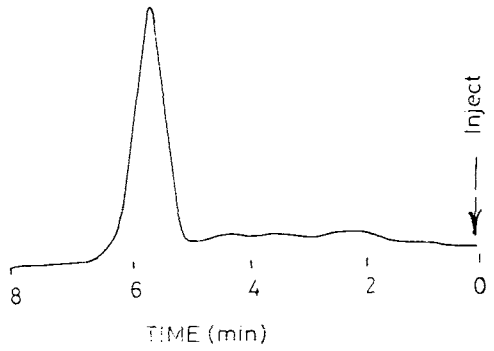

Figure 3 GPC trace of TDI–HEMA–β-CD.

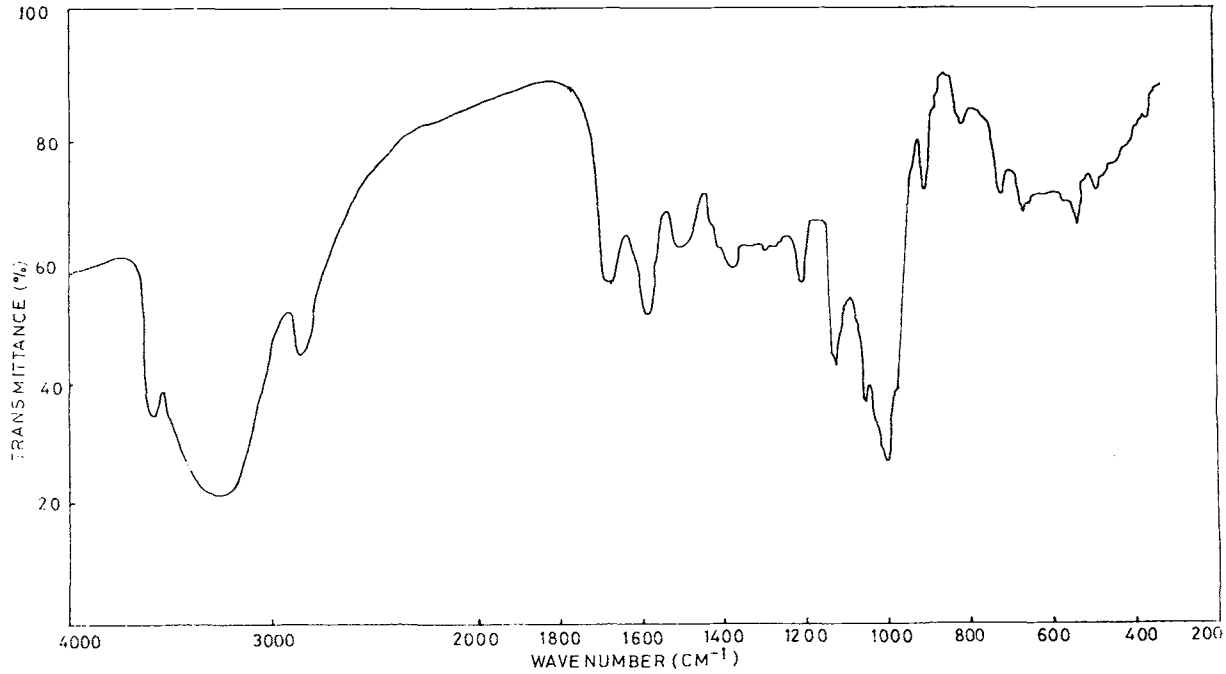

Figure 4 ATR–IR spectrum of PU grafted with modified β-CD.

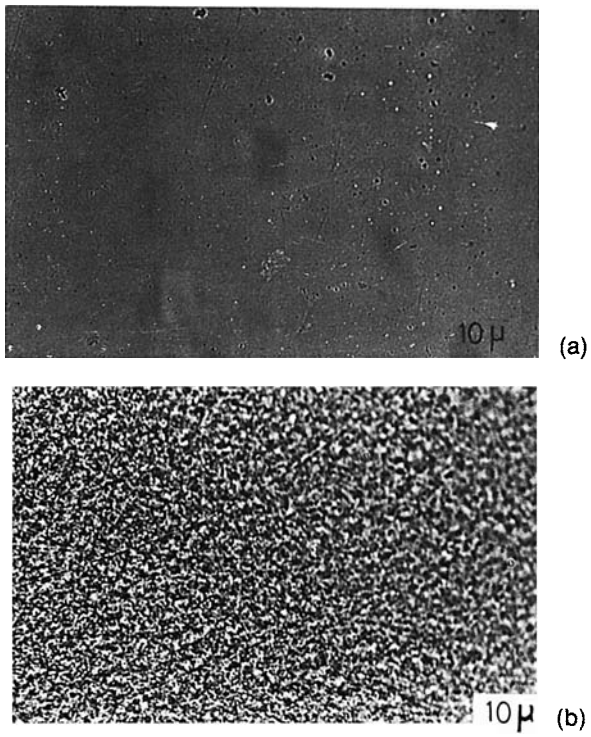

Figure 5 SEM micrograph of (A) PU and (B) PU grafted with modified β-CD.

orientation of the soft segment along with stress together with the hard/soft segment ratio.[10] The bulky β-CD can indeed interfere the orientation possibility of soft-segment chains. In that sense, the ultimate stress–strain parameters of the modified PU would have been much lower if the grafting was deep in the bulk.

It seems that β-CD modified with HEMA can be grafted easily to polymeric substrates. The modification is nearly confined to the surface, and due largely to this surface, features could be altered simultaneously, preserving most of the other bulk characteristics of the substrate polymers.

Preliminary studies to evaluate the affinity of modified polyurethane toward specific components is carried out by keeping the PU strips (modified

Table I Stress–Strain Parameters of Control and Modified PU

Material	Stress (kg/cm^2)	Strain (%)
PU	520 ± 10	496 ± 6
Modified PU	440 ± 7	378 ± 5

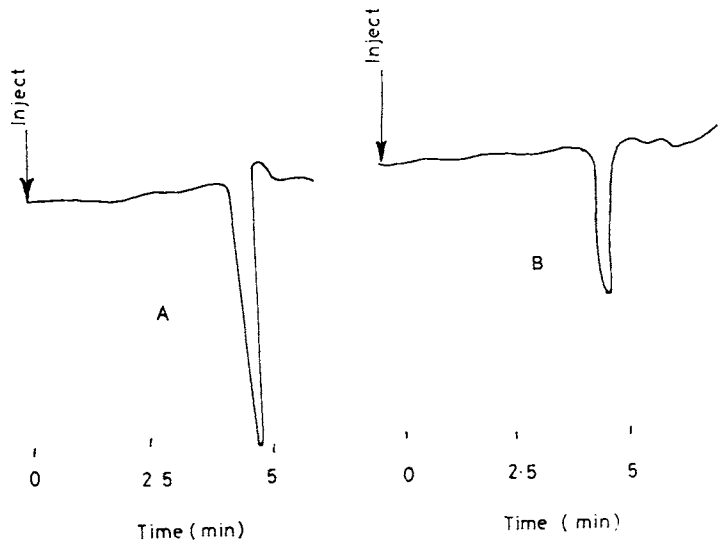

Figure 6 Chromatographic trace of (A) phenol : water mixture and (B) phenol : water mixture containing modified PU. Volume injected = 20 μL.

and control) in a phenol : water mixture for 30 min under a static condition. Figure 6(A) and (B) depict the chromatographic traces of the solutions before and after exposure to the polymers. The amount of phenol absorbed from the solution by the polymers was estimated using the chromatographic data and a calibration plot for phenol. It is interesting to point out that control PU absorbs just 5 wt % phenol while modified PU absorbs 43% phenol from the solution [see Fig. 6(B)]. The considerable difference between these values reflect the profound influence of the modification. Detailed studies to explore the modification process to develop membranes of varied types will be reported in a forthcoming publication.

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