

Transparent Organic Materials Made from Copolymerization of Styrene with Urethane-Methacrylate Macromer. I. Monomacromer System

YONGJIN LI,¹ GONGSHAN WANG,² DEYUE YAN¹

¹ College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

² Department of Polymer Materials Science and Engineering, College of Material Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China

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ABSTRACT: Urethane macromers were prepared by reacting tolylene diisocyanate with various glycols, followed by end capping with 2-hydroxyethyl methacrylate in the presence of dibutyltin dilaurate as the catalyst. Various proportions of styrene to the urethane-methacrylate macromer were adopted to cure at 70°C for 7–8 h. The effect of the composition on the properties was systematically studied. These transparent materials exhibited excellent mechanical and optical properties and heat deflection temperature. All of the copolymer sheets had a transmittance similar to the poly(methyl methacrylate) sheet and had a rather high refractive index. The mechanical and thermal properties varied with the ratio of styrene to macromer and with the kind of glycol used in the synthesis of the macromer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 348–357, 2001

Key words: urethane-methacrylate macromer; transparent polymeric materials; mechanical properties; transmittance; refractive index

INTRODUCTION

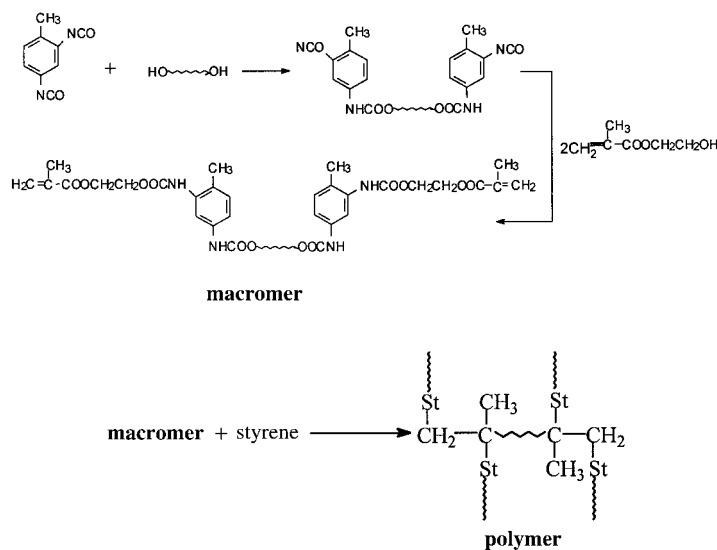
Transparent polymeric materials, such as poly(methyl methacrylate) (PMMA) and polycarbonate (PC), are widely used for many applications including sign boards, carports, and automobile parts, as well as optical applications (e.g., compact disks, optical lenses, and fibers).¹ However, some inferior properties of these polymers, for instance, the low heat resistance of PMMA² and

the poor optical properties of PC,³ often limit their use. Therefore, the development of new amorphous polymers with excellent optical properties, high heat resistance, and good mechanical properties was expected.

Thermoset polymers copolymerized from urethane-methacrylate with vinyl monomers are used in many fields including coatings, printing inks, sealants, and adhesives.^{4–6} It is well known that thermoset polymers have high thermal stability and good surface hardness.⁷ In the present work, a new class of transparent material was fabricated by crosslinking styrene with urethane-methacrylate macromer. The reaction schemes of the synthesis processes for the macromer and the material can be depicted as follows:

Correspondence to: D. Yan (dyyan@mail.sjtu.edu.cn).
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The macromer without glycol was prepared by reacting 1 mol tolylene diisocyanate (TDI) with 2 mol 2-hydroxyethyl methacrylate (HEMA; the first step of the reaction). Other macromers were prepared by reacting 1 mol of TDI with 0.5 mol glycol, followed by end capping with 1 mol HEMA. Styrene was used as a solvent during the first reaction step and the reaction was monitored using the volumetric method. Two types of poly(ethylene glycol) (PEG) with molecular weights of 400 and 1000 (PEG400 and PEG1000) were used to synthesize the macromers. Then the macromer and styrene were cured at 70°C for about 8 h (i.e., the second step of the reaction). The series of materials prepared from glycol free, PEG400, and PEG1000 with various styrene contents (i.e., 50, 60, 70, and 80%) were designated as SU1, SU2, and SU3, respectively.

EXPERIMENTAL

Materials

The 80/20 mixture of 2,4/2,6-TDI (E. Merck), styrene (Fluka), dibutyltin dilaurate (DBTL, Fluka), HEMA (Fluka), and PEG (Fluka) were used as received. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform.

Methods

Preparation of Macromer and Precured Syrups

The reaction of TDI with glycol and HEMA was carried out in the presence of a stoichiometric amount of styrene. During the first step of the reaction the styrene acted as a solvent. Then AIBN was dissolved in the second part of the styrene, which was added into the reaction system after the macromer was prepared.

A typical procedure for the preparation of syrups (e.g., in the SU2 the MW of the PEG is 400 and the styrene content is 50%) is described below. A mixture of 13 g of HEMA (0.1 mol), 20 g of PEG400 (0.05 mol), 17.4 g of TDI (0.1 mol), and 30 g of styrene was put into a three-necked flask fitted with a water condenser and a nitrogen inlet. The reaction was carried out at 40°C for 1–1.5 h. Then a few drops of DBTL were added into the solution and the reaction temperature was increased to 60°C for 2 h. Subsequently, 20 g of styrene containing 0.4 g of AIBN (0.4% w/w) was added to the reaction system. Then the syrup was complete.

Preparation of Mold and Curing of Material

Two 200 × 300 × 5 mm glass plates were cleaned with chromic acid, water, and acetone, which was followed by drying. The glass plates were sprayed

with silicone and then covered with two pieces of poly(ethylene terephthalate) film to release the mold. A 3-mm thickness rubber gasket, which was cut into a U shape, was placed between the plates, which were held together using steel clamps. One side of the glass plate was kept open to pour in the macromer syrup.

One hundred milliliters of macromer syrup was poured into the mold. The opening side of the mold was then closed using a metal plate and clamps.

The filled mold was then placed into an air oven at 70°C for 7–8 h, after which it was cooled to ambient temperature. The clamps were then removed, and the transparent sheet was taken out and used for testing the properties.

IR Spectra

The IR spectra were obtained with a Perkin-Elmer FTIR spectrometer.

Optical Properties

The percentage of light transmittance of the sheet in the wavelength range of 200–800 nm was measured using a Perkin-Elmer Lambda 3B UV-visible spectrophotometer. The refractive indices of the samples were measured using an Abbe refractometer (ASTM D542). Three 30 × 20 × 3 mm specimens were used for testing, and an average value was reported.

Mechanical Properties

Tensile strength measurements were carried out at room temperature employing an Instron material tester (mode 4206) at a crosshead speed of 5 cm/min according to ASTM D638. Notched Izod impact tests were conducted at room temperature with a Ceast impact tester according to the ASTM D526 standard. The Rockwell hardness was measured according to ASTM D785.

Thermal Property

The heat deflection temperature was measured by means of an HDT & VPST tester according to ASTM D648.

Other Properties

The density and water absorption were determined according to ASTM standards.

RESULTS AND DISCUSSION

The IR spectra of the reactant mixture, macromer syrup, and curing material are shown in Figure 1. The macromer syrup has very weak absorption at 2270 cm⁻¹, which belongs to the stretching vibration of —NCO; therefore, —NCO and —OH reacted in the preparation of the macromer. However, carbon-carbon double bonds in residual HEMA groups were essentially not polymerized at this stage, which was confirmed by the IR spectrum where strong characteristic absorptions at 1650 and 890 cm⁻¹ were assigned to the double bond of the MA and =CH₂ wagging vibrations, respectively. In contrast, we could not find these carbon-carbon double bonds and —NCO absorption bands in the IR spectrum of the final materials, which meant that they were completely crosslinked after curing.

The crosslinking density is a very important parameter to influence the properties of the material. For convenience sake, an equation to calculate the crosslinking density was introduced as follows in this work:

$$P = \frac{\rho(1 - \gamma)}{2M_{\text{TDI}} + M_{\text{PEG}} + 2M_{\text{HEMA}}} \quad (1)$$

where P is the crosslinking density of the material (i.e., the mole number of crosslink points per unit volume, mol/cm³), ρ is the density of the material (g/cm³), γ is the weight percentage of styrene, and M is the molecular weight of each raw material (g/mol). In accordance with eq. (1), P decreases with increasing γ and M_{PEG} .

Figure 2 shows the tensile strength of the material. With increasing styrene content, it can be observed that the tensile strength decreases for sample SU1 and increases for SU3. However, for sample SU2, there is a maximum tensile strength at a certain styrene content (about 60%). The tensile strength of polystyrene is higher than that of polyurethane with long soft chains, so the larger the styrene content in the sample, the higher the tensile strength. On the other hand, the crosslinking density decreases with increasing styrene content [as shown in eq. (1)]. These two opposite effects result in a maximum of the tensile strength for SU2 at a certain styrene content.

The typical stress-strain curves for copolymers of the three series materials with 50% styrene

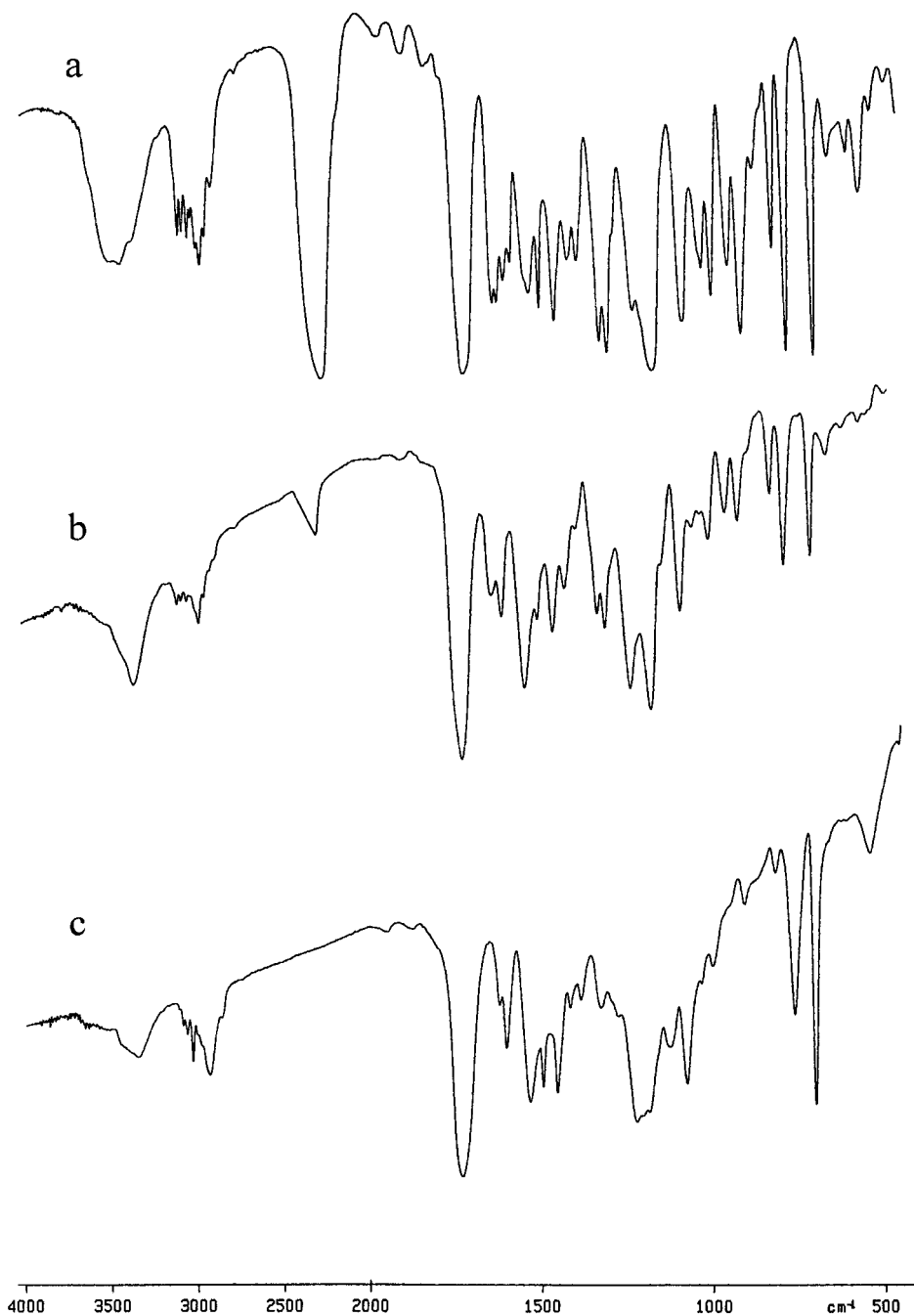


Figure 1 FTIR spectra of the mixture of reactants for the first reaction step (spectrum a), the macromer syrup (spectrum b), and the material after curing (spectrum c; SU1 with 50% styrene content).

content are shown in Figure 3. With increasing the molecular weight of PEG, the maximum tensile stress decreases, and the shape of the curves varies. Sample SU3 with 50% styrene content shows a typical ductile fracture, and sample SU1 with 50% styrene content shows a typical brittle

fracture. This indicates a gradual change in the fracture mechanism from brittle to ductile upon increasing the molecular weight of the glycol, which is attributed to the increase in flexibility of the copolymer introduced by the PEG moiety of the macromers.

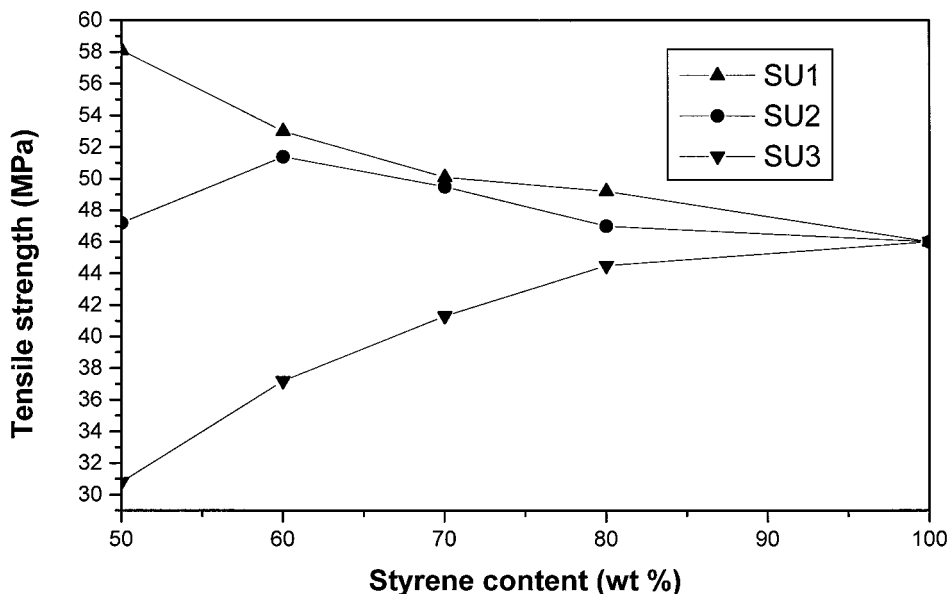


Figure 2 The tensile strength of the materials as a function of the styrene content for SU1, SU2, and SU3.

The dependence of the impact strength of the material on the styrene content is shown in Figure 4. It can be observed that the impact strength of SU1 is much lower than those of SU2 and SU3. This is due to the rigid structure and the high crosslinking density for SU1. We also find that

there is a maximum strength at a certain styrene content (about 60%) for the SU1, which may result from the moderate crosslinking effect.⁸ This means that, for the polymer with the rigid molecular chain, a certain degree of crosslinking can increase the interaction of the molecular chains;

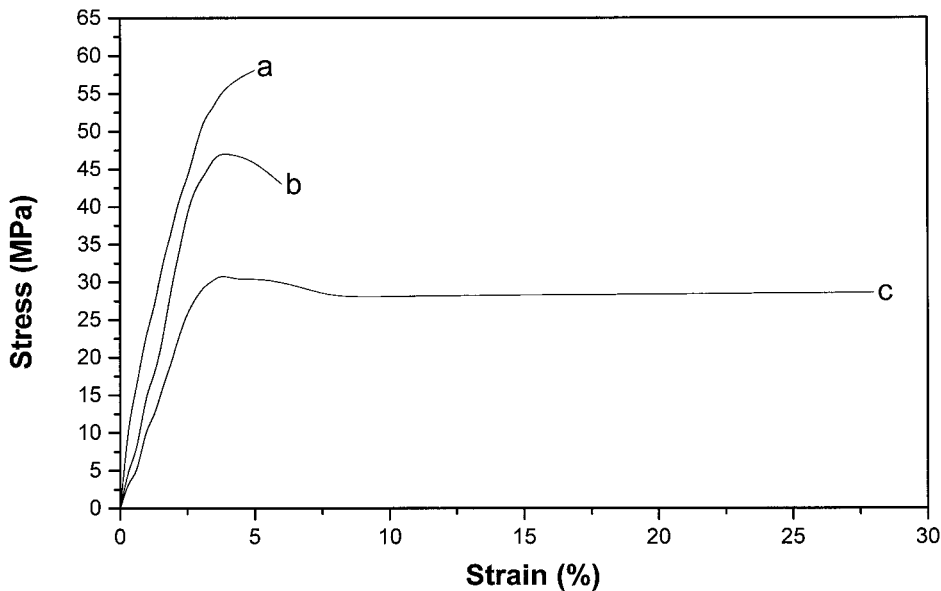


Figure 3 The strain-stress plot of the materials: SU1 with 50% styrene content (curve a), SU2 with 50% styrene content (curve b), and SU3 with 50% styrene content (curve c).

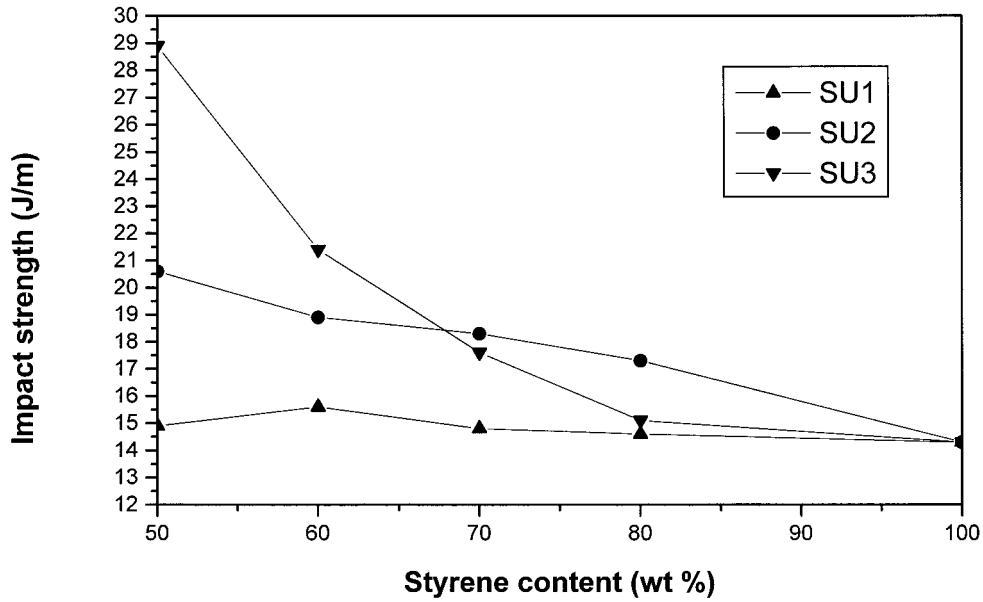


Figure 4 The impact strength of the materials as a function of the styrene content for SU1, SU2, and SU3.

therefore, the impact strength increases. But too much crosslinking density hinders the movement of the chains, and the impact strength will decrease. The segment of sample SU1 is especially rigid, so there is a maximum impact strength with the increasing of the styrene content. For samples SU2 and SU3 the crosslinking density is

relatively low; therefore, the soft chain content exerts an important influence on the impact strength. The impact strength decreases strikingly with increasing styrene content.

The main factors that affect surface hardness are the soft segment content and the crosslinking density. Larger hard-soft segment ratios

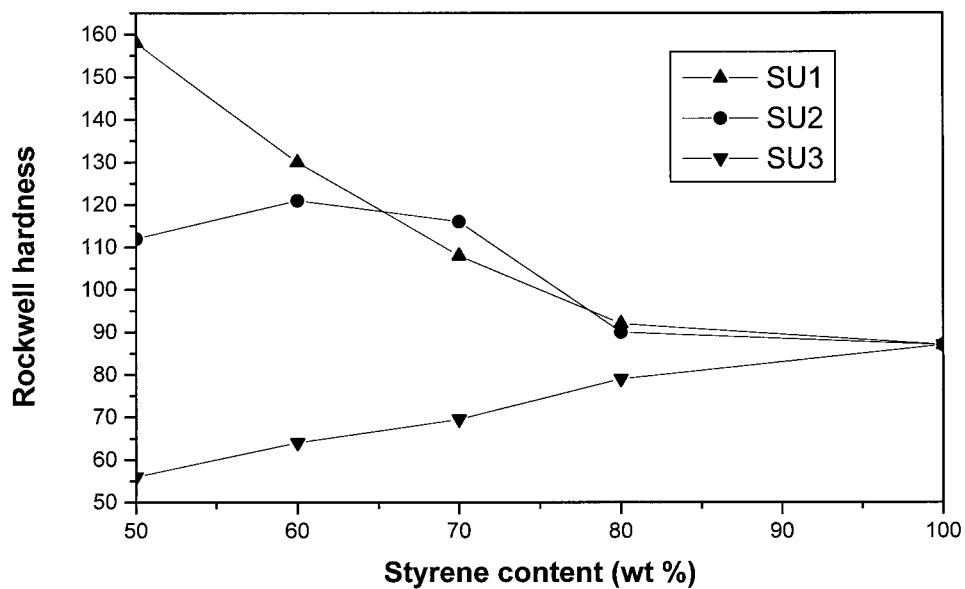


Figure 5 The Rockwell hardness of the materials as a function of the styrene content for SU1, SU2, and SU3.

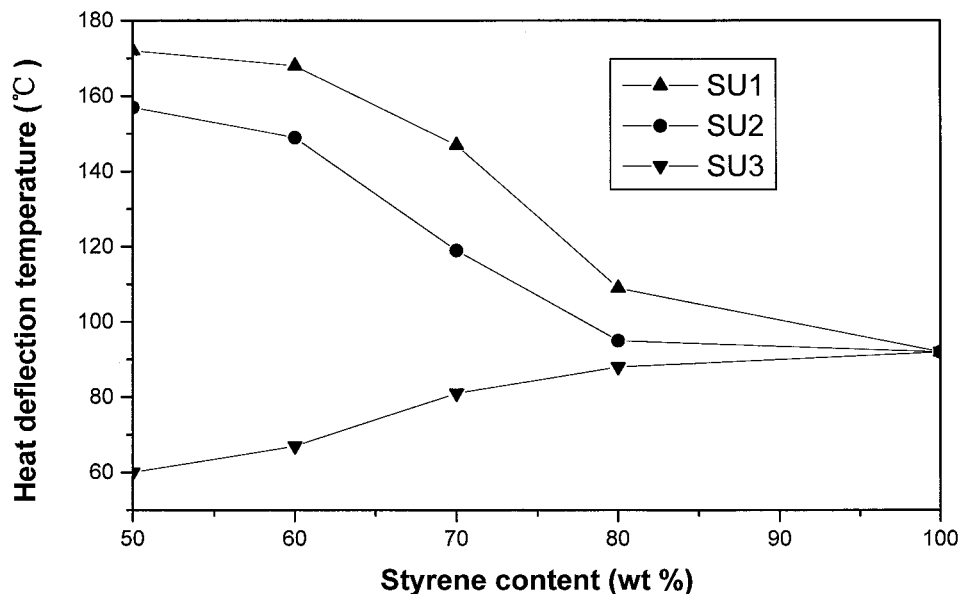


Figure 6 The heat deflection temperature of the materials as a function of the styrene content for SU1, SU2, and SU3.

and higher crosslinking densities gave materials with higher surface hardness. The Rockwell hardness of the material is shown in Figure 5 and that of PMMA is 98. With increasing styrene content, the hardness of SU1 is deteriorated because of lower crosslinking density.

However, that of SU3 is enhanced because of the larger hard-soft segment ratios. For sample SU2 the hardness has a maximum value at a certain styrene content (about 60%). These trends are similar to those of the tensile strength (as shown in Fig. 2).

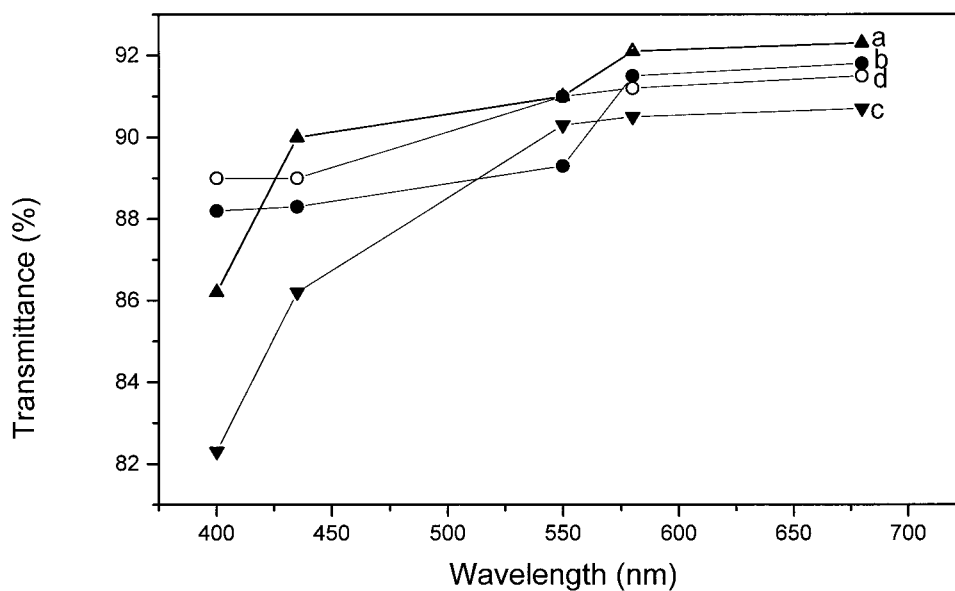


Figure 7 The histograms of the percentage of transmittance versus the wavelength for the materials: SU1 with 50% styrene content (curve a), SU2 with 50% styrene content (curve b), SU3 with 50% styrene content (curve c), and PMMA (curve d).

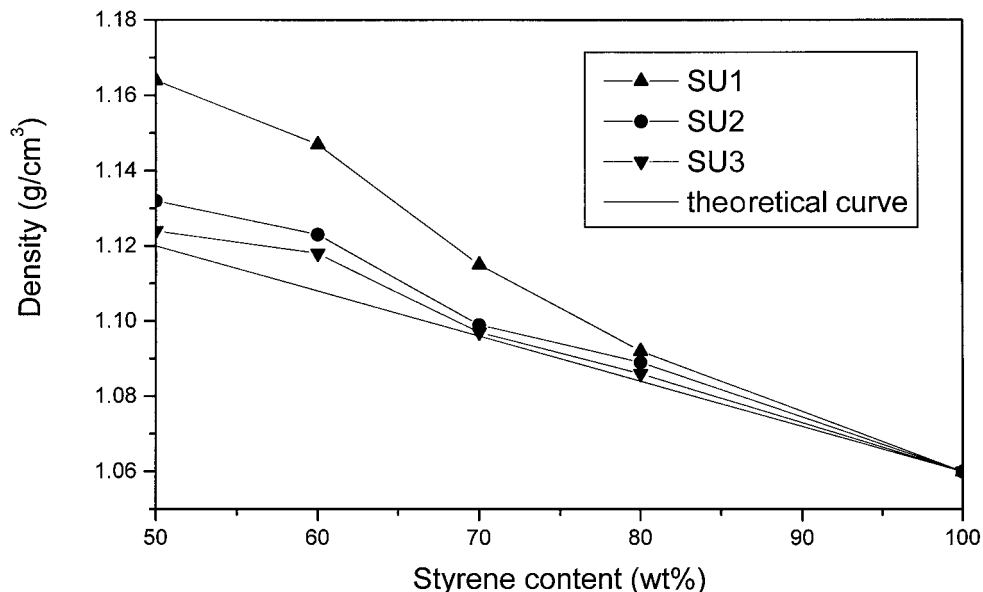


Figure 8 The theoretical density and the measured density of the material as a function of the styrene content for SU1, SU2, and SU3.

It is obvious that the high crosslinking density hinders the movement of molecular chains, and the movement of hard chains is more difficult than that of soft chains. So sample SU1 has a much higher heat deflection temperature than SU2 and SU3 (Fig. 6). The crosslinking density and the heat deflection temperature decrease with increasing sty-

rene content for sample SU1 whereas the content of soft chains $-\text{CH}_2\text{CH}_2\text{O}$ decreases and the heat deflection temperature increases with increasing styrene content for sample SU3. Surprisingly, SU2 also has relatively high heat resistance and its heat deflection temperature decreases with increasing styrene content, just like that of SU1.

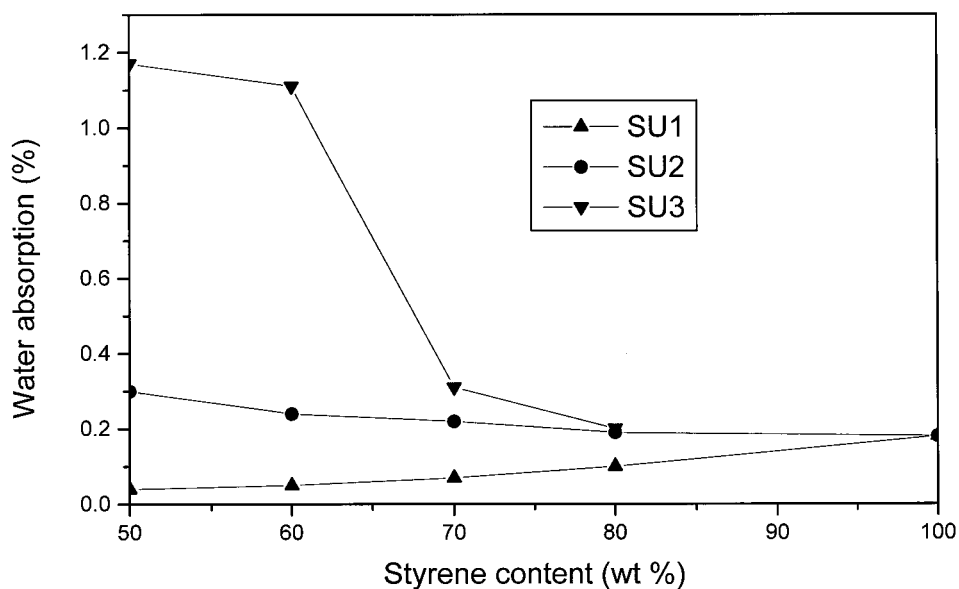


Figure 9 The water absorption of the material as a function of the styrene content for SU1, SU2, and SU3.

Table I Properties of Sample with 50% Styrene Content

Property	SU1	SU2	SU3	PMMA
Tensile strength (MPa)	58.1	47.2	30.8	60.7
Izod impact strength (J/m)	14.9	21.2	28.9	20.8
Rockwell hardness (—)	148	112	52	98
Heat deflec. temp. (°C)	172	157	60	95
Transmittance (%)	91.5	91.2	91.0	92.0
Refractive index (—)	1.598	1.578	1.555	1.492
Density (g/cm ³)	1.16	1.13	1.12	1.19
Water absorption (%)	0.04	0.34	1.17	2.0

The histograms of the percentage of transmittance versus the wavelength for various copolymer sheets are given in Figure 7. All the copolymer sheets have a transmittance similar to the PMMA sheet in the wavelength range of 400–800 nm. But sample SU1 has higher transmittance than the PEG system. The reason may be attributed to the high irregular molecular chains because of the high crosslinking density. The PEG system has much more —CH₂CH₂O chains and they can aggregate to form small domains, which can decrease the transmittance of the materials.

The refractive index is an important parameter for transparent materials, especially for optical lens applications. The lens thickness can be reduced considerably if a transparent material with high refractive index is used. When the styrene content is 50%, the refractive indices for SU1, SU2, and SU3 were found to be 1.589, 1.578, and 1.555, respectively, while that of PMMA was 1.492. With the increasing of the styrene content and decreasing of the molecular weight of the glycol the refractive index increases.

The theoretical equation⁹ for the calculation of the copolymer density is as follows:

$$\frac{1}{\rho} = \frac{W_1}{\rho_1} + \frac{W_2}{\rho_2} \quad (2)$$

where ρ is the density of the material; w_1 and w_2 are the percentage of styrene and macromer, respectively; and ρ_1 and ρ_2 are the density of pure polystyrene and pure polymacromer, respectively.

The theoretical density and the measured density of the material are given in Figure 8. The structure of the material is rather compact because of the high crosslinking density, so the real density is higher than the theoretical one.

Water absorption is an undesirable property for optical plastics, because it leads to low dimensional stability. The water absorption of the material shown in Figure 9 is lower than that of PMMA. The water absorption of SU1 is much lower than that of the PEG system, which can also be attributed to higher crosslinking density and lower content of polar groups of —CH₂CH₂O—.

The properties of the polymer with 50% styrene content are summarized in Table I; those of PMMA appear in the last column. The light transmittance of the materials was almost the same as that of PMMA, and the refractive index was much higher. SU1 showed excellent thermal resistance, high tensile strength, and low water absorption and SU3 displayed high Izod impact strength. However, SU2 had a good balance of these properties.

CONCLUSIONS

It can be concluded from these studies that a new transparent polymeric material can be fabricated by copolymerization of styrene with urethane-MA macromers. The mechanical, optical, and other properties of the resulting materials were carefully investigated. The typical materials obtained from the optimized conditions possessed excellent mechanical and optical properties, which were much better than those of PMMA. In addition, all of the properties varied with the content of styrene and the glycol used in the preparation of the macromers. Therefore, we can produce organic transparent materials with appropriate properties according to the application purpose.

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