

# Transparent Organic Materials Made from Copolymerization of Styrene with Urethane-Methacrylate Macromer. II. Macromer Mixture System

YONGJIN LI,<sup>1</sup> GONGSHAN WANG,<sup>2</sup> DEYUE YAN<sup>1</sup>

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

<sup>2</sup> 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:** A urethane-methacrylate (UM) macromer mixture was prepared by reacting tolylene diisocyanate with a mixture of 1,4-butylene glycol (as the rigid glycol) and poly(ethylene glycol), followed by end capping with 2-hydroxyethyl methacrylate. The transparent polymeric material was fabricated by copolymerizing the macromer mixture with styrene. The effects of the styrene content and the composition of the macromer mixture on the properties were studied. The results showed that the material displayed a unique balance of excellent transparency, high heat resistance, good impact strength, and low water absorption, especially when the soft macromer (UM2) content was 20 or 40%. The visible light transmittance was more than 90%, and the refractive index was much higher than that of poly(methyl methacrylate). All properties were extensively regulated according to practical demand. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 674–679, 2001

**Key words:** transparent polymeric material; mechanical properties; refractive index; transmittance; heat deflection temperature

## INTRODUCTION

Generally speaking, linear polymers have good impact strength and excellent processability; however, because of their thermoplasticity, their heat resistance and surface hardness are limited.<sup>1</sup> Thermoset polymers, on the other hand, have higher heat resistance and surface hardness.<sup>2</sup> Therefore, one can fabricate high heat resistance and excellent surface hardness polymeric materials by preparing crosslinking polymers.

A new class of transparent thermoset polymer was fabricated in previous work<sup>3</sup> by crosslinking pure urethane-methacrylate (UM) macromers with styrene. The properties of the materials were systematically studied. Materials prepared by rigid macromers had high tensile strength, good surface hardness, and superior heat resistance, but their impact strength was not very good. In contrast, the polymers made from soft macromers showed outstanding impact strength, but some other properties (i.e., heat deflection temperature and Rockwell hardness) could not fully meet the demands. Thus, a mixture of rigid macromer and soft macromer was used to prepare transparent materials and a good balance of heat resistance, surface hardness, and impact strength of the materials was expected.

Correspondence to: D. Yan (dyyan@mail.sjtu.edu.cn).

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## EXPERIMENTAL

## Materials

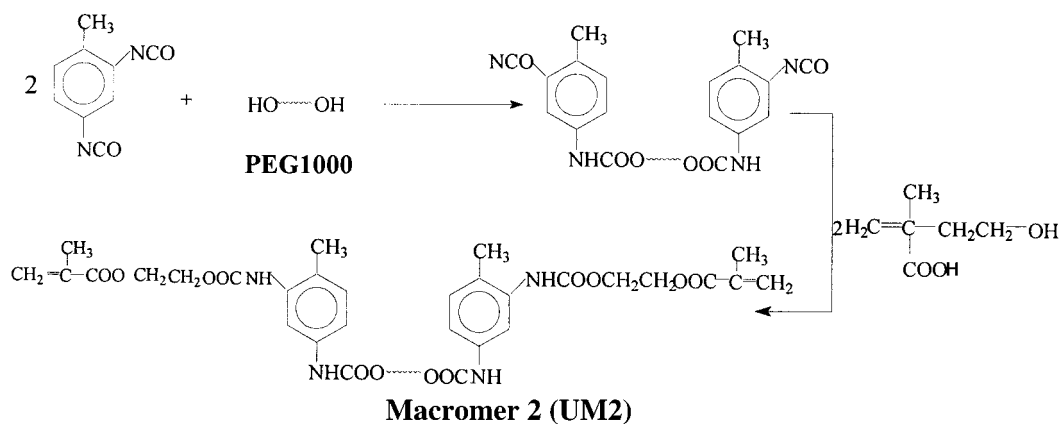
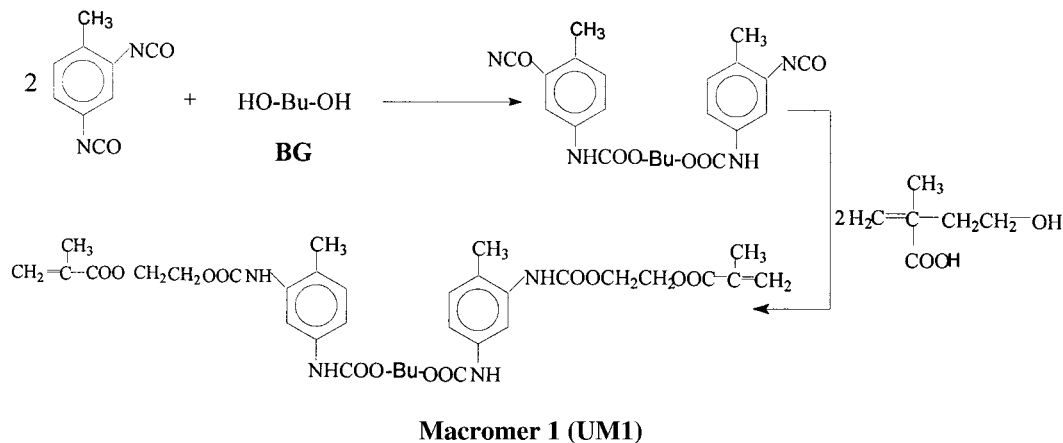
The components in an 80/20 mixture of 2,4/2,6-tolylene diisocyanate (TDI, E. Merck), styrene (Fluka), dibutyltin dilaurate (DBTL, Fluka), 2-hydroxyl methacrylate (HEMA, Fluka), 1,4-butylene glycol (BG, Fluka), and poly(ethylene glycol) (molecular weight of 1000, PEG1000, Fluka) were used as received. Azobisisobutyronitrile (AIBN) was recrystallized from chloroform.

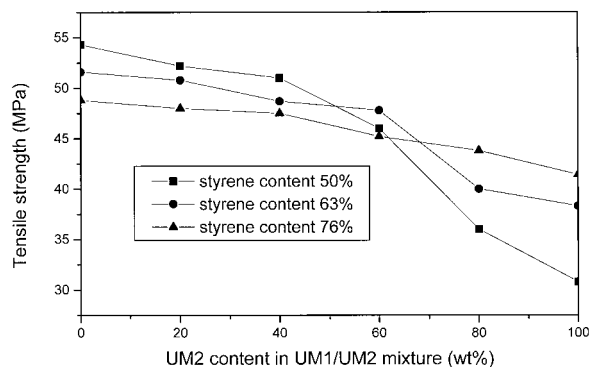
## Preparation of Macromer and Precured Syrups

The reaction structure of the synthesis processes for the macromer mixture and the final materials can be depicted as follows:

The reaction of TDI with the glycol mixture and HEMA was carried out in the presence of the stoichiometric 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 mixture was prepared.

The weight ratio of the two glycols should be properly regulated to make the content of UM2 in the macromer mixture 20, 40, 60, and 80% (w/w). Various styrene contents (i.e., 50, 63, and 76%) in the system were used in the investigation. A typical procedure for the preparation of the syrups (e.g., UM2 content = 20% in the macromer mixture and styrene content in whole system = 50%) is described below. A mixture of 20.24 g of HEMA (0.1557 mol), 6.22 g of PEG1000 (0.0062 mol),



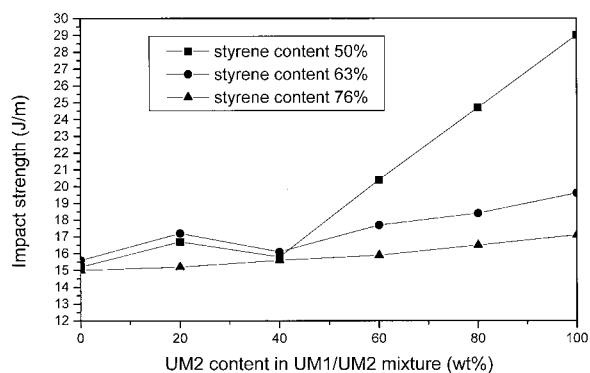


**Figure 1** The tensile strength of the materials as a function of UM2 at three styrene contents.

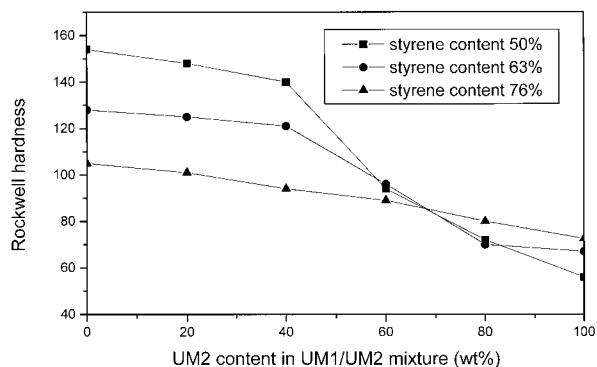
6.44 g of BG (0.0716 mol), 27.10 g of TDI (0.1557 mol), and 40 g of styrene was put into a three-necked flask fitted with a water condenser and a nitrogen inlet. The reaction was carried out at 40°C for 2–2.5 h. Then a few drops of DBTL were added into the solution and the reaction temperature was increased to 60°C for 2 h. Subsequently, 20 g of styrene containing 0.48 g of AIBN (0.4% w/w) was added to the reaction system.

#### 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 spray and then were covered with two pieces of poly(ethylene terephthalate) film to release the mold. A 3 mm thick U-shaped rubber gasket was placed between the plates, and the plates were held together using steel clamps. One side of the glass plate mold was kept open for pouring the macromer syrup.



**Figure 2** The impact strength of the materials as a function of UM2 at three styrene contents.



**Figure 3** The Rockwell hardness of the materials as a function of UM2 at three styrene contents.

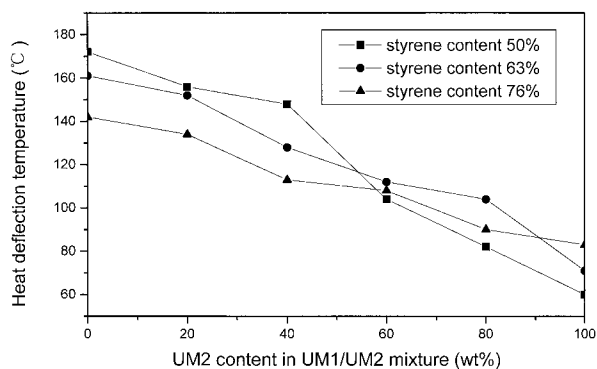
One hundred milliliters of the macromer syrup was poured into the mold. The opening side of the mold was then closed using a metal plate and clamps.

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

#### Characterization and Testing

##### Optical Properties

The percentage of light transmittance of the sheet in the wavelength range of 400–800 nm was measured by using a Perkin–Elmer Lambda 3B UV-visible spectrophotometer. The refractive indices of the samples were measured by using an Abbe refractometer (ASTM D542). Three 30 × 20 × 3 mm specimens were used for testing, and an average value was reported.



**Figure 4** The heat deflection temperature of the materials as a function of UM2 at three styrene contents.

**Table I Transmittance and Refractive Index of Samples with 50% Styrene Content**

	UM2 Content (%)					
	0	20	40	60	80	100
Transmittance (%)	91.5	91.6	92.0	91.5	91.1	91.0
Refractive index	1.60	1.60	1.61	1.59	1.61	1.56

### Mechanical Properties

Tensile strength tests were carried out at room temperature by employing an Instron material tester (mode 4206) at a crosshead speed of 5 cm/min according to ASTM D638; Izod impact tests were conducted at room temperature with a Ceast impact tester (code 6545/000) according to the ASTM D526 standard. The Rockwell hardness was measured according to ASTM D785.

### Thermal Properties

The heat deflection temperature was measured by means of an HDT&VPST tester.

### Other Properties

The density was determined according to ASTM D1505, and water absorption was measured by the 2-h boiling immersion method according to ASTM D570.

## RESULTS AND DISCUSSION

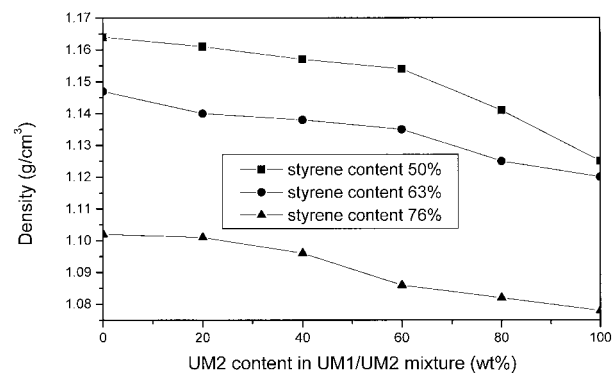
The factors that affected the tensile properties of the material were the ratio of hard to soft segments in the material, the styrene content, and the crosslink density. Larger hard to soft segment ratios and higher crosslink density gave the material a higher tensile strength. So the tensile strength of the material decreased with increasing UM2 content in the macromer mixture (as shown in Fig. 1). But when the content of UM2 in the macromer mixture was less than 40%, the tensile strength did not decrease dramatically. This indicated that introducing a small amount of soft macromer into the materials did not strikingly deteriorate the tensile strength.

The impact strengths of copolymers made from different compositions are shown in Figure 2. The existence of soft segments greatly improved the impact properties of the material. We also found

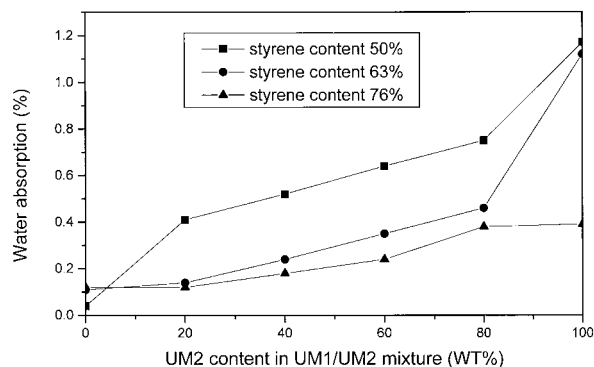
that the samples made from 50 and 63% styrene content had surprisingly high impact strength when the UM2 content in the macromer mixture was 20%. This abnormally high impact strength could be due to the moderate crosslinking effect because of the high crosslinking density. On the contrary, the samples made from 76% styrene showed gradually increasing impact strength with increasing UM2 content. Compared with the tensile strength of the material, the samples made from 20% UM2 had high tensile strength and good impact strength.

In general, the material containing long soft segments had low surface hardness. But, as shown in Figure 3, no dramatic decrease of the Rockwell hardness was observed when the UM2 content was lower than 40% in the macromer mixture. This trend was also similar to that of the tensile strength (Fig.1).

Heat resistance is a very important property for plastics, especially for transparent polymers. In fact, the low heat resistance property of poly(methyl methacrylate) (PMMA) often limits its uses, in spite of its excellent optical properties such as high transparency, large Abbe number, and low birefringence. Figure 4 shows the effect of UM2 content in the macromer mixture on the



**Figure 5** The density of the materials as a function of UM2 at three styrene contents.



**Figure 6** The water absorption of the materials as a function of UM2 at three styrene contents.

heat deflection temperature. It can be seen from the figure that the heat deflection temperature decreased gradually with increasing UM2 content. This was attributed to the low crosslinking density and large amount of soft  $-\text{CH}_2\text{CH}_2\text{O}-$  segments. However, just like the tensile strength and Rockwell hardness, the decrease of heat deflection temperature was not very sharp when the UM2 content was lower than 40% in the macromer mixture.

The transmittance and the refractive indices of the materials are shown in Table I. All samples had good optical properties. It can also be found that the material made from the macromer mixture had higher transmittance than that of the material made only from UM2 and lower than that of the material made only from UM1. This may be due to the lower chain order of the macromer mixture system than that of the UM2 system. The refractive indices were also higher than that of PMMA, which is 1.49.

The density of the material is shown in Figure 5. With increasing UM2 content, the crosslink

density decreased and the arrangement of the chain became looser, so the density of the material decreased accordingly.

The water absorption of the material was lower than that of the PMMA, which is 2.0% (shown in Fig. 6). The water absorption of the material increased with an increase of the UM2 content and a decrease of the styrene content.

The properties of the polymers with 50% styrene content are summarized in Table II; those of PMMA appear in the last column. The materials displayed intermediate properties compared to the monomacromer system. Therefore, we can alternate the properties by changing the two macromers' ratio and styrene content. The light transmittance of the materials was almost the same as that of PMMA, and the refractive index was much higher. The tensile strength and the heat resistance of the samples made from the macromer mixture were a little lower than that of the material made from the monomacromer, but the impact strength was higher.

## CONCLUSIONS

A transparent polymeric material with a good balance of optical, thermal, mechanical, and low water absorption properties was prepared based on a UM macromer mixture. The sample with a styrene content of 50% and a UM2 content in the macromer mixture of 20% showed the best properties. The transparency was almost on the same level as that of PMMA, and the heat deflection temperature was higher than that of PMMA by 80°C. This polymer also had high impact strength, which was also a little higher than that of PMMA. The tensile strength was also accept-

**Table II** Properties of Samples with 50% Styrene Content

	UM2 Content (%)						PMMA
	0	20	40	60	80	100	
Izod impact strength (J/m)	15.2	16.7	15.8	20.4	24.4	28.9	20.8
Rockwell hardness	153	148	140	94	72	56	98
Heat deflec. temp. (°C)	171	156	148	104	82	60	95
Tensile strength (MPa)	54.3	52.2	51.0	46.1	35.9	30.8	60.7
Transmittance (%)	91.5	91.6	92.0	91.5	91.1	91.0	92.0
Refractive index	1.60	1.60	1.61	1.59	1.61	1.56	1.49
Density (g/mL)	1.16	1.16	1.16	1.15	1.14	1.12	1.19
Water absorption (%)	0.04	0.41	0.52	0.64	0.76	1.17	2.0

able, although it was not greater than that of PMMA. At the same time, the properties of the material could also be regulated by varying the rigid to soft macromer ratio and the styrene content according to practical demands.

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