

Transparent Organic Materials Made from Copolymerization of Styrene with Urethane-Methacrylate Macromer. III. Thermal Behaviors

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ABSTRACT: Urethane-methacrylate macromers were prepared by the reaction of tolylene diisocyanate with various glycols, followed by end capping with 2-hydroxyethyl methacrylate. A new transparent polymeric material was fabricated by the copolymerization of the macromers with styrene. The thermal behaviors of the new material were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis. The samples with different distances between crosslinking points exhibited different thermal behaviors. The sample with short segments between the crosslinking points had a homogenous phase structure and displayed only one glass transition. For the sample with long segments between the crosslinking points, there was a major glass transition and a minor relaxation at high temperature. Surprisingly, the sample with moderate length segments between the crosslinking points showed a novel exothermic peak in the DSC curve. The exothermic peak may have resulted from the formation of a special physical interaction, such as a hydrogen bond. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 680–686, 2001

Key words: urethane-methacrylate macromer; thermal behavior; hydrogen bond; differential scanning calorimetry; dynamic mechanical analysis

INTRODUCTION

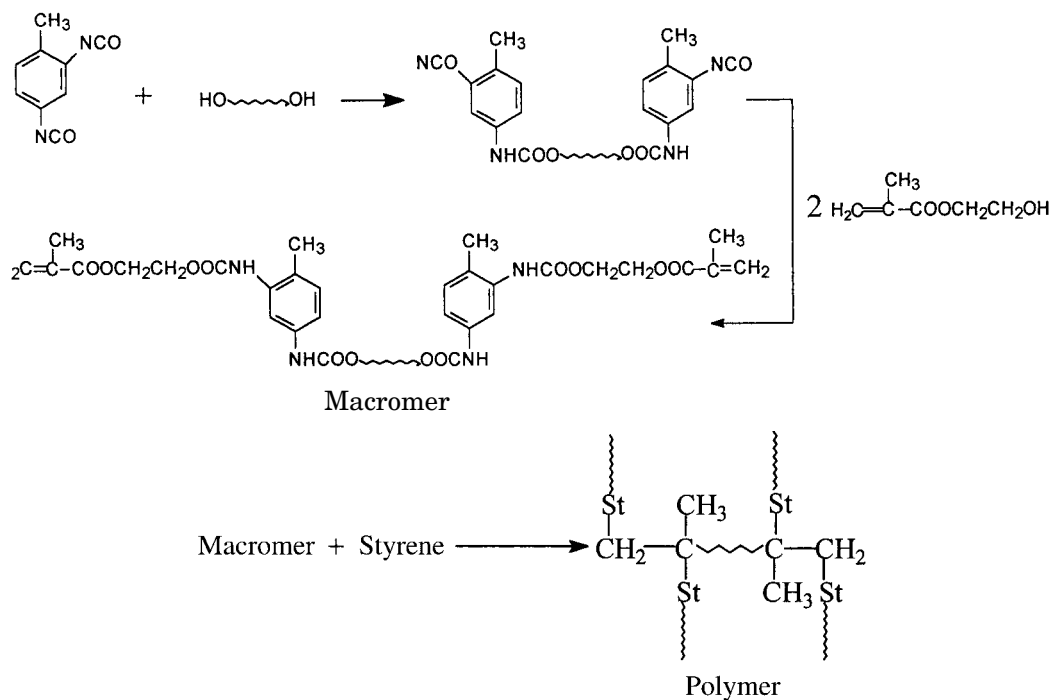
Macromer copolymerization technology is widely used in the modern synthesis industry.¹ Urethane-methacrylate (UM) macromer is a typical kind of macromer and it was extensively investigated as photo, radiation, or laser curable coatings, printing inks, and adhesives.^{2–5} However,

its potential applications in other fields attracted a lot of interest in recent years. In a previous work⁶ new transparent polymeric materials were prepared by copolymerization of styrene with the UM macromer. The effects of the styrene content and the molecular weight (MW) of glycol on the physical, optical, and other properties were studied systematically. In addition, the transparent polymeric materials made from macromer mixtures were also fabricated and studied.⁷ In the present work the thermal behaviors of the copolymer made from monomacromer were carefully investigated.

The reaction schemes of both the macromer and material synthesis can be depicted as follows:

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1,4-Butylene glycol (BG, MW 90) and three poly(ethylene glycol) (PEG) oligomers (PEG200, PEG400, and PEG600) with different MWs (i.e., 200, 400, and 600) were used to prepare the macromers. The samples made from the four glycols were accordingly designated as SU90, SU200, SU400, and SU600. The styrene content in all of the samples was 50% (w/w).

EXPERIMENTAL

Materials

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

Preparation of Macromer and Precured Syrups

The reaction of TDI with glycol 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 was prepared.

A typical procedure for the preparation of syrups (e.g., SU400) 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 was 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 ready.

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

One hundred milliliters of macromer syrup was poured into the mold. The opening side of the

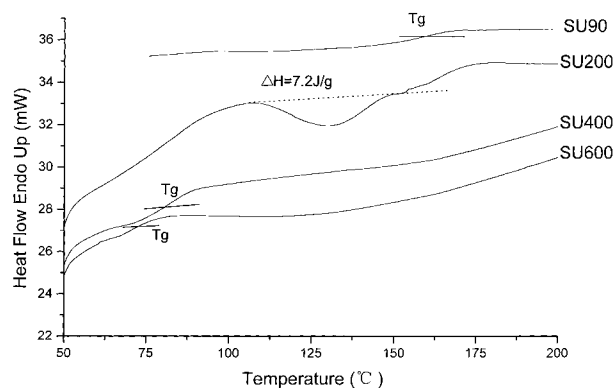


Figure 1 DSC traces of the four samples.

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 and characterization.

Characterization and Testing

IR Spectra

The Fourier transform IR (FTIR) spectra of the materials were measured by using a KBr pelletting technique and a Nicolet 520 FTIR spectrometer was used.

Differential Scanning Calorimetry (DSC)

The glass-transition temperature (T_g) of the materials was determined by using a Perkin–Elmer DSC 7 thermal analyzer system. All samples were tested at a heating rate of 10°C/min under dry N_2 gas (25 mL/min) over a temperature range from room temperature to 200°C.

Dynamic Mechanical Analysis (DMA)

The DM properties of the material were characterized using a Perkin–Elmer DMA 7e DM analyzer. The specimens were tested in three-point bending to determine the glass transition. The frequency was 2 Hz and the temperature range was 10–200°C. The T_g was determined from the maximum peak value of the $\tan \delta$ curve.

RESULTS

DSC thermograms of the samples are shown in Figure 1. We found only one glass transition for

the SU90, SU400, and SU600 samples and the T_g values were 157, 84, and 78°C, respectively. Comparing SU400 and SU600 with SU90, a subtle difference can be observed (i.e., the slopes of the DSC base lines of the former slightly increase at about 150°C). Surprisingly, we could not find any distinctive glass transitions for the SU200 sample, as shown in Figure 1; however, a novel exothermic peak was observed at around 130°C during the DSC scan and the exotherm was about 7 J/g.

Figure 2 presents DMA curves for the four samples. In good agreement with the DSC analysis, the DMA curve also displayed only one loss peak at 156°C for the SU90 sample. There was also a main glass transition at 82 and 78°C for the SU400 and SU600 samples, respectively. Unlike the SU90 sample, a small transition was also observed for the two samples at about 150°C, which may correspond with the slight increase of the DSC base line slope. However, the DMA curve of the SU200 showed a broad loss peak and two transition temperatures (at 90 and 140°C), which was similar to the typical half-compatible polymer blend behaviors.

Several additional experiments were implemented to investigate the mechanism of the novel exothermic peak for the SU200 sample. Because the exothermic peak of the sample was around 130°C, the sample was heat-treated at 140°C for 2 h and then the DSC test was carried out again (as shown in Fig. 3). The exothermic peak disappeared and there was only one glass transition in the DSC curve. The IR spectra for the original and heat-treated samples are displayed in Figure 4. No apparent difference was found between the two IR spectra. However, some absorption bands

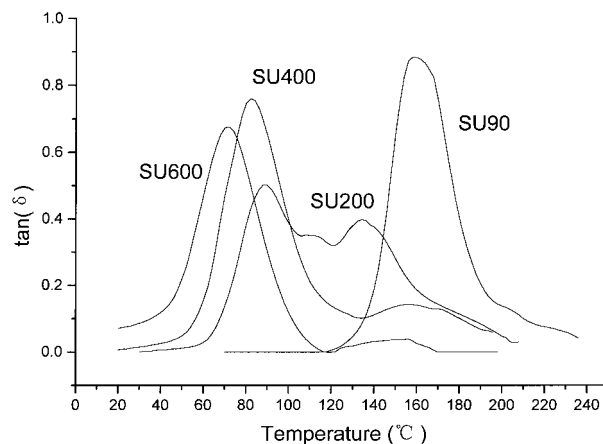


Figure 2 DMA traces of the four samples.

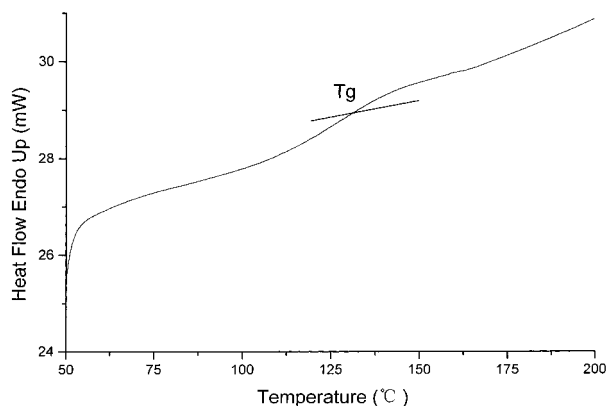


Figure 3 A DSC trace of the heat-treated SU200 sample.

of the heat-treated sample were finer than those of the original sample. The —NH stretching vibration of the original sample was located at 3351

cm^{-1} ; however, the vibration band shifted to 3328.6 cm^{-1} after heat treatment. For comparison, the SU400 sample was also treated with the same procedure. We did not detect any difference between the two IR spectra (see Fig. 5).

DISCUSSION

Theoretically, the copolymerization of the two components used in this work can form a relatively regular 3-dimensional network because the UM macromer has two double bonds and the styrene has only one double bond. Thus, we can describe the schematic architecture of the material as shown in Figure 6.

The segments of the heavy lines in Figure 6 are the polyurethane (PU) segments and those of the thin lines are the polystyrene (PS) segments. For

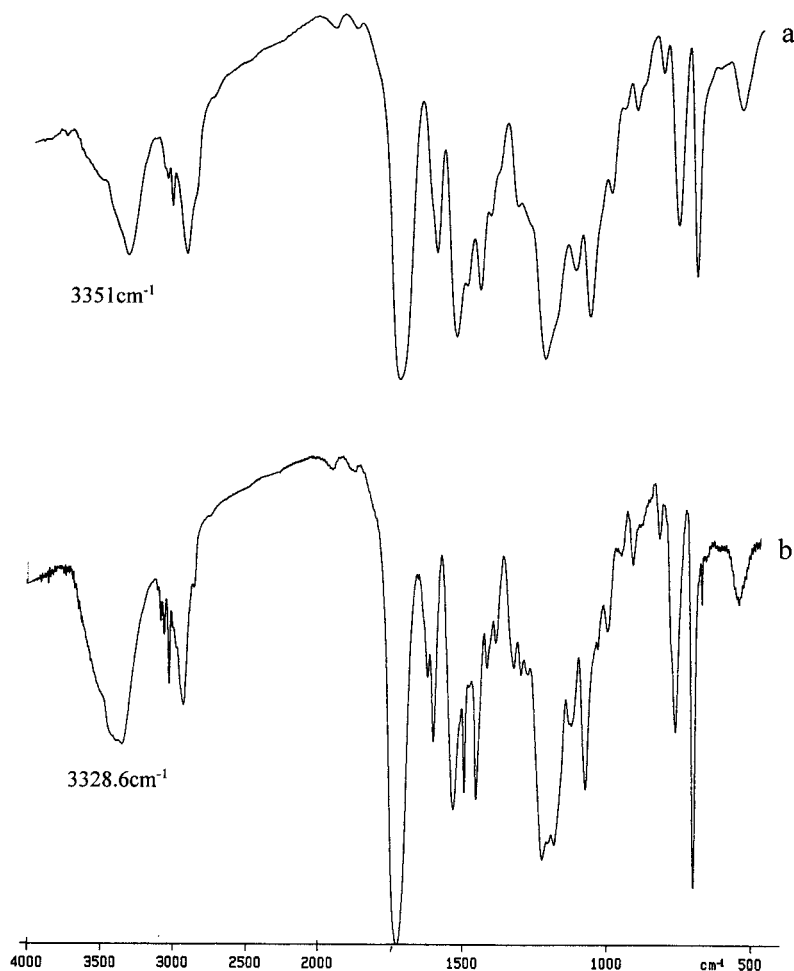


Figure 4 IR spectra of SU200: (a) the original sample and (b) the sample heat treated at 140°C for 2 h.

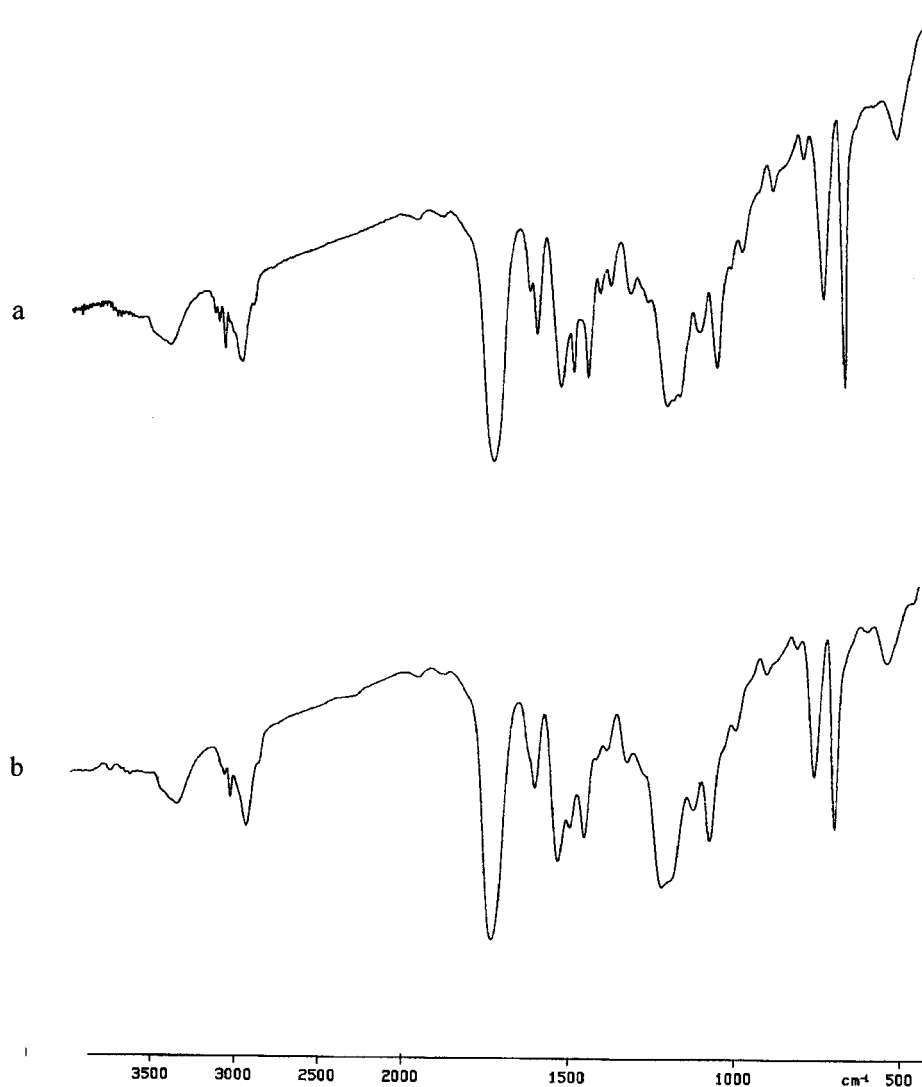


Figure 5 IR spectra of SU400: (a) the original sample and (b) the sample heat treated at 140°C for 2 h.

sake of convenience, the crosslinking density can be calculated as follows:

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

where P is the crosslinking density (the number of moles of the crosslinking points per unit volume, mol/mL); ρ is the density of the material (g/mL); γ is the weight percentage of styrene in the material; and M_{TDI} , M_{glycol} , and M_{HEMA} are the molecular weights of TDI, glycol, and HEMA, respectively.

We can also estimate the average MW of the bulk segments (which are also PU segments) between two adjacent crosslinking points:

$$M_U = 2M_{\text{TDI}} + M_{\text{glycol}} + 2M_{\text{HEMA}} \quad (2)$$

Consequently, the average MW of the thin segments (i.e., PS segments) between two adjacent crosslinking points can be calculated in terms of the following equation:

$$M_{\text{St}} = \frac{\rho\gamma}{2P} = \frac{\rho\gamma(2M_{\text{TDI}} + M_{\text{glycol}} + 2M_{\text{HEMA}})}{2\rho(1 - \gamma)} \quad (3)$$

It is obvious from eqs. (1), (2), and (3), that the M_U and M_S increase and the P decreases when increasing the glycol molecular weight but keeping the γ constant. That is to say, the lengths of the

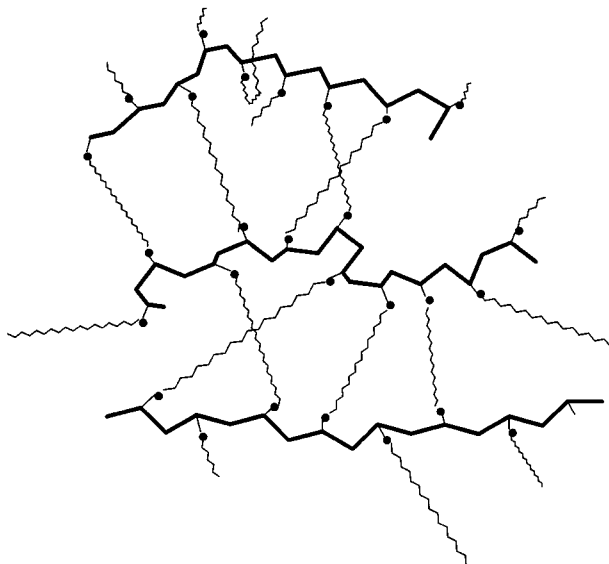


Figure 6 A schematic diagram of the crosslinking architecture for the materials. The heavy lines are the polyurethane segments and the thin lines are the polystyrene segments.

PU and PS segments between adjacent crosslinking points increase.

The SU90 sample had a high crosslinking density and very short segments between crosslinking points because of the low MW of the BG. The segment mobility is strongly constrained by chemical crosslinking bonds when the distance between crosslinking points is smaller than a certain length.⁸ Therefore, the high crosslinking density of the SU90 made the material have a good homogenous phase; consequently, the DSC and DMA analysis displayed only one glass transition and the T_g was relatively high. As far as PEG400 and PEG600 are concerned, the crosslinking density of the materials was much lower and the length between crosslinking points was also much longer. In the meantime, PS and PEG segments were compatible with each other in the crosslinking system according to a previous study.⁹ So the two samples showed distinctive glass transitions at about 80°C in their DSC and DMA curves. On the other hand, the movement of the segment attached to the crosslinking points was more difficult because of the limitations of the crosslinking. With increasing temperature, a relaxation took place for these segments. Therefore, we detected an increase in the slope of the DSC base line and a small loss peak in their DMA curves at about 157°C, which also corresponds to the T_g of the SU90 sample.

Very surprisingly, the SU200 sample displayed completely different thermal behaviors. There was a novel exothermic peak in the DSC curve (as shown in Fig. 1), and the DMA curve was also different from the other samples (as shown in Fig. 2). For the SU200 sample, the crosslinking density was not very high and the lengths of the PU and PS segments were not very short because of the moderate molecular weight of the glycol used according to eqs. (1)–(3). Therefore, the movement of the segments was much easier than that in the SU90 sample and a little more difficult than that in the SU400 and SU600 samples. The exothermic peak may have resulted from a kind of special interaction between the molecular chains and the hydrogen bond is a common interaction for PU. Thus, we think this special interaction may be the H bonds between the —NH groups and —COO groups. The crosslinking density for SU90 was very high and the segment length was very short, so the movement of the segments was so difficult that the —NH and —COO groups could not reach each other. Consequently, the interaction could not take place. Therefore, no exothermic peak was found in its DSC curve. For SU400 and SU600 samples, the content of the —NHCOO groups was very low and the heat effect was rather weak. Moreover, the movement of the segments was much easier and the H bond may have been formed at low temperature, so the exothermic peak may not be detected in their DSC curves.

In contrast, because of the moderate flexibility of the segment for the SU200 samples, the segments could move when the temperature was increased during the DSC measurements. So —NHCOO groups can rotate and move accordingly, and the —NH and —COO groups between different —NHCOO groups may get close to form H bonds, resulting in an exothermic peak. However, the exothermal enthalpy was not very high (about 7 J/g) because it was a physical interaction. Meanwhile, the phase structure was also changed because of the special interaction. The broad loss peak with two relaxations in the DMA curve also corresponded to the movement of the two kinds of segments.

For the sample treated at 140°C for 2 h, no exothermic peak was observed in its DSC measurement because of the H bond formed in the process of the heat treatment. On the other hand, because of the formation of this special interaction, the original separating structure converted into one homogenous phase and it had only one T_g (as shown in Fig. 3). In the meantime, the IR

spectra of the original and heat-treated samples convinced us that the novel exothermic peak was due to a kind of special physical interaction (perhaps the H bonds). Therefore, no chemical reaction took place in the process of the heat treatment because no apparent difference between the two IR spectra and no new absorption bands were observed after the heat treatment. However, the absorption peaks became finer, which meant that the molecular structure became ordered during the heat treatment. At the same time, the shift of the —NH stretching vibration band from 3351 to 3328 cm^{-1} implied the formation of hydrogen bonds. Besides, the 3328 cm^{-1} band was a little broader than that of the 3351 cm^{-1} band, which reflected a reasonably wide distribution of hydrogen bond distances for the heat-treated sample. Further studies about this phenomenon are underway in our laboratory.

CONCLUSIONS

The copolymers of styrene with UM macromers showed distinctively different thermal behaviors because of its special crosslinking structure. Especially for the SU200 sample, a novel exothermic peak was observed in its DSC curve. We attributed the special exotherm to the formation of a

special physical interaction between the polar groups and the formation of the ordered microscopy molecular structure. We also proposed that the special interaction may be the hydrogen bonds.

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