*Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 1163-1166*

# DDSC STUDIES ON POTMG/PMMA BLENDS AND POTMDM-*net*-PMMA

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## Abstract

Thermal behaviors of POTMDM-*net*-PMMA and POTMG/PMMA blends were studied by DDSC. $T_g$ of the polymer network was lowered by increasing the POTMDM in feed for copolymerization of POTMDM and MMA. A crystallization peak was observed only when MMA in feed was less than 30%. $T_g$ of POTMG/PMMA was also lowered by decreasing the content of PMMA, however, the change was observed only when PMMA content was more than 70%. These results suggest that thermal transitions of the polymer network are restricted by the mesh size. POTM chains of the polymer network effectively play as a plasticiser.

**Keywords:** DDSC, glass transition, polymer blend, polymer network, poly(oxytetramethylene)

## Introduction

Poly(oxytetramethylene)glycohol (POTMG) and its analogues (POTM) are the unique polymers because of its low melting point and crystallization behaviors. Recently, much attention has been paid to the thermal behaviors of polymer blends and polymer networks consisting with POTM [1–4]. Poly(oxytetramethylene}dimethacrylate-*net*-poly(methyl methacrylate) (POTMDM-*net*-PMMA) is an interesting system to study the interactions between POTM and PMMA chains in the network structure. We report the thermodynamic behaviors of POTMG/PMMA blend and POTMDM-*net* PMMA studied by DDSC.

## Experimental

### *Materials*

As POTMG, TERATANE 2900$^R$ was obtained from Aldrich and used as received. PMMA was obtained from Kanto Chemicals. The synthetic procedure of POTMDM was previously reported [3]. The identification of the product was done by JASCO 230 FTIR and Bruker DMX-500 NMR. The copolymerization of POTMDM with MMA was carried out in a flame sealed 12 mm diameter glass tube. The samples were photo-irradiated for 10 h by 450 W high pressure mercury lamp (<300 nm). The ratios in feed for POTMDM to MMA were 3:1, 2:1, 1:1, 1:2, and 3:1. Swelling of these polymer networks was measured in acetone, and confirmed

*1418–2874/99/ $ 5.00*

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that the swelling is proportional to MMA in feed for the preparation. Polymer blends of POTMG and PMMA were prepared from their chloroform solution.

### *Method*

DDSC curves of both polymer blends and polymer networks were obtained by Perkin Elmer DSC 7 in Iso-Scan mode. The temperature control program was as follows: raising the temperature by a 2 K step at 7.5 K $min^{-1}$ following isothermal stage for 20 s. The measurements were carried out in the range from 233 to 413 K. Each sample was heated up to 413 K and then cooled at 200 K $min^{-1}$ to 233 K. Obtained heat-flow curve was divided into real part (storage $C_p$ curve) and imaginary part (loss $C_p$ curves). Original heat-flow curve was converted to a total $C_p$ curve that corresponds to conventional DSC curve.

## Results and discussion

On DDSC curves of all POTMG/PMMA blends in Fig. 1, the storage $C_p$ curve showed both an endothermic peak that can be assigned to melting of POTMG crystalline and a step change that is glass transition. On the loss $C_p$ curve, a small broad peak was observed near the step change temperature on storage $C_p$ curve. DDSC curves of POTMDM-*net*-PMMA in Fig. 2 showed a step change on the storage $C_p$ curves when MMA in feed was more than 30 wt%. When MMA was less than 30%, both an endothermic peak and a step change were observed on storage $C_p$ curve. Peak temperatures on DDSC curves were plotted *vs.* the PMMA or MMA in feed in Fig. 3. The $T_m$ of both blends and network fell down with increasing PMMA concentration. The network polymer showed a lower $T_m$ than polymer blends at the same PMMA concentration.

Enthalpy change of POTM crystalline melting $\Delta H_m$ in polymer blends and polymer networks were calculated from total $C_p$ curve. The results were plotted *vs.* PMMA concentration in Fig. 4. The network polymer showed smaller $\Delta H_m$ than the polymer blend at the same PMMA content. The $\Delta H_m$ should be proportional to

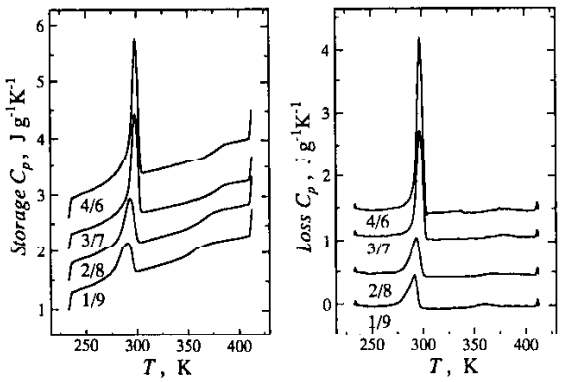


**Fig. 1** DDSC curves of all POTMG/PMMA blends. a) storge $C_p$ curves; b) loss $C_p$ curves

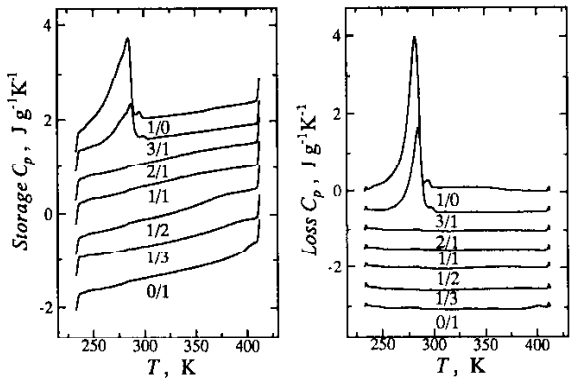


**Fig. 2** DDSC curves of all POTMDM-*net*-PMMAs. a) storage $C_p$ curves; b) loss $C_p$ curves

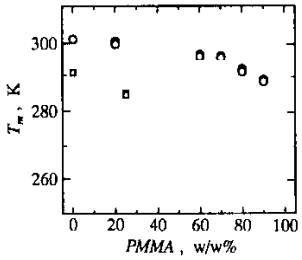


**Fig. 3** Peak temperature on DDSC curves. Peak on storage $C_p$ curves: POTMG/PMMA (•); POTMDM-*net*-PMMA (■). Peak on loss $C_p$ curves: POTMG/PMMA (○); PTMDM-*net*-PMMA (□)

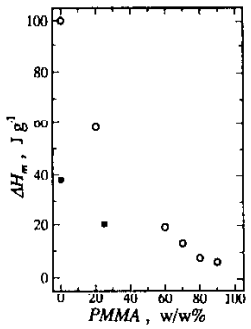


**Fig. 4** Enthalpy change of melting calculated from total $C_p$ curve: POTMG/PMMA (○) and POTMDM *net* PMMA (■)

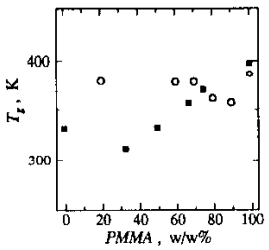


**Fig. 5** Glass transition temperature of POTMG/PMMA (o) and POTMDM-*net*-PMMA (■)

POTM crystalline phases and its crystallinity in the samples. Since the amount of crystalline phase or crystallinity of the polymer network is expected to be lower than the polymer blend, these results suggest that structure of POTMDM-*net*-PMMA be more homogeneous than POTMG/PMMA. Since PMMA chains in the polymer network are directly connected to the POTM chains, conformation and distance of POTM chains should be more restricted in the polymer network than in the polymer blend. The small $\Delta H_m$ and low $T_m$ of polymer networks compare with the polymer blends can be considered as the products of the network structure.

Glass transition temperature of POTMDM-*net*-PMMA and POTMG/PMMA was obtained from storage $C_p$ curves. The results were plotted *vs.* their PMMA concentration in Fig. 5. $T_g$ of polymer blend is sometimes compared with theoretical equations. The Fox equation [5] and the Pochan equation [6] have been tested. Pochan plots are shown in Fig. 5 using $T_g$=187 K for POTMG [1]. In polymer blends, the $T_g$ data only fitted the theoretical line when PMMA concentration was more than 75 wt%. POTMG and PMMA may be miscible at high PMMA concentration but interaction between these two are weak. The $T_g$ of the polymer network did not fit the theoretical lines, but fell down by decreasing MMA in feed. The change was almost linear and the range was obviously wider than POTMG/PMMA. These data were between polymer blend and theoretical lines. At low PMMA concentration, less than 30 wt%, the $T_g$ obviously became higher than expected. Since melting transition also observed in this PMMA concentration range, decrease of the mesh size of the polymer network may increase the ununiformity of the network structure.

These results suggest that both melting and glass transition are restricted by the network structure. POTM and PMMA chains in the polymer network interact through covalent bond each other. POTM in the polymer network effectively plays as a plasticizer.

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