THERMAL ANALYSIS OF POLYMER NETWORKS CONSISTING OF DIFFERENT HOMOPOLYMERS
Poly(methacrylic acid)-*net*-poly(oxytetramethylene)

T. Kojima, M. Tsuchiya and K. Tago

Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka-SHI 239, Japan

Abstract

TG and DSC were carried out on PMAA-net-POTM in order to elucidate the relation between the heterogeneity and the thermal changes; moreover, TG and DSC were carried out on PPOTMDM and PMAA to compare the results. The onset temperature in the last stage in the TG curve of PMAA-*net*-POTM increases as the concentrations of DMF and POTMDM in the polymerization decrease. This is explained in terms of plasticizers effects. A single peak due to fusion of POTM chains appears in the DSC curves of most copolymers. However, it is not seen in the DSC curves of copolymers with high heterogeneity. This is explained in terms of the freezing of POTM chains by frozen heterogeneous moieties.

Keywords: DSC, heterogeneity in polymer network, poly(methacrylic acid)-*net*-poly(oxytetramethylene), thermogravimetry

Introduction

Recent studies [1–4] on polymer networks demonstrated that thermodynamic properties are influenced by heterogeneity due to cross-links. However, strict relations between the heterogeneity and the properties are difficult to elucidate because of the small scale of the heterogeneous moiety. The heterogeneity is considered to show up more clearly for polymer networks consisting of homopolymers with different properties, such as the polymer networks formed by the copolymerization of poly(methacrylic acid) (PMAA) with poly(oxytetramethylene)dimethacrylate (POTMDM). Differences in thermal transition temperature between PMAA and POTM (the glass transition temperature [5] of PMAA is at about 500 K and the melting point [6] of POTMDM is at about 300 K) lead us to expect that the thermal analysis data are influenced by the heterogeneity of PMAA-*net*-POTM. In previous work [7], considerable effects of heterogeneity on swelling behaviour were found for PMAA-*net*-POTM.

The object of the present work was to elucidate the relationship between thermodynamic properties and heterogeneity for PMAA-*net*-POTM with various PMAA/POTM compositions by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). For comparison, TG and DSC data on POTM glycol (POTMG) and POTMDM homopolymer were also obtained.

Experimental

The copolymerization of MAA with POTMDM was carried out in a flame-sealed 20 mm diameter glass tube containing benzoyl peroxide (BPO) as initiator and N,N-dimethylformamide (DMF) as solvent. The amounts in the feed ranged from 9.5×10^{-3} to 2.4×10^{-2} mol for MAA, from 3.3×10^{-5} to 8.5×10^{-4} mol for POTMDM, from 2.1×10^{-6} to 2.3×10^{-4} mol for BPO, and from 2.2×10^{-3} to 2.2×10^{-2} mol for DMF. The duration and the temperature of copolymerization were 24 h and 333 K, respectively. The feed composition for polymerization is summarized in Table 1.

Table 1 Composition in feed of polymerization

Copolymer	Amount in feed/mol			
	MAA	POTMDM	BPO	DMF
1	9.5×10^{-3}	9.4×10^{-5}	9.5×10^{-6}	9.5×10^{-3}
2	1.7×10^{-2}	8.5×10^{-4}	1.7×10^{-5}	1.7×10^{-2}
3	1.7×10^{-2}	3.3×10^{-5}	1.7×10^{-5}	1.7×10^{-2}
4	2.3×10^{-2}	2.3×10^{-4}	2.3×10^{-4}	2.3×10^{-2}
5	2.1×10^{-2}	2.0×10^{-4}	2.1×10^{-6}	2.1×10^{-2}
6	1.2×10^{-2}	1.2×10^{-4}	1.2×10^{-5}	4.8×10^{-3}
7	1.8×10^{-2}	1.7×10^{-4}	1.8×10^{-5}	0

The synthesis of POTMDM was carried out by an esterification procedure, using POTMG and an excess of fresh methacryloyl chloride. POTMDM was purified by reprecipitation from acetone solution by addition of methanol. The product was identified as POTMDM *via* the appearance of the absorption due to the C=O stretching vibration in the infrared spectrum obtained with a JEOL 230 FTIR spectrophotometer, and *via* the disappearance of the absorption due to the proton of the OH group in the NMR spectrum obtained by the CP/MAS technique with a Bruker DMX-500 NMR instrument.

PPOTMDM and PMAA were synthesized by bulk polymerization in a flame-sealed glass tube at 333 K for 24 h. The initiator used was BPO.

All samples were used without purification, to maintain the heterogeneity in them.

Thermal analysis was carried with a Perkin-Elmer 7 series thermal analysis system.

Results and discussion

Thermogravimetry

The TG curves of PMAA-*net*-POTM are a mix of the TG curves of PMAA and PPOTM, as shown in Fig. 1. The mass loss of MAA occurs in three stages: vaporization of unpolymerized MAA, dehydration from two carboxyls, and decomposition of PMAA anhydride. In the TG curve of PPOTMDM, the mass loss at 430 K
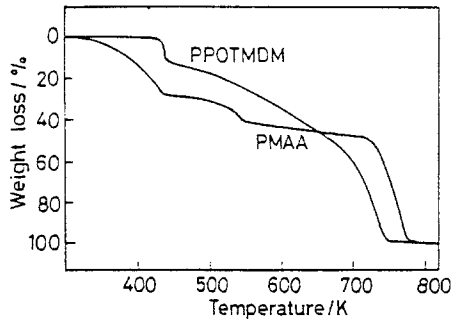
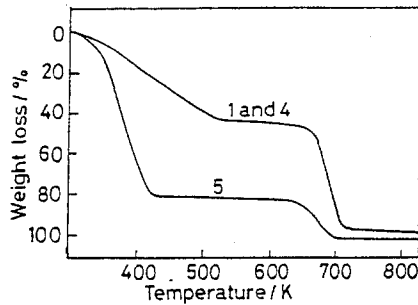**Fig. 1** TG curves of PPOTMDM and PMAA

Fig. 2 TG curves of copolymers 1, 4 and 5. BPO/MAA/g/g: 4, 0.028/1.0; 1, 0.0028/1.0; 5, 0.00028/1.0
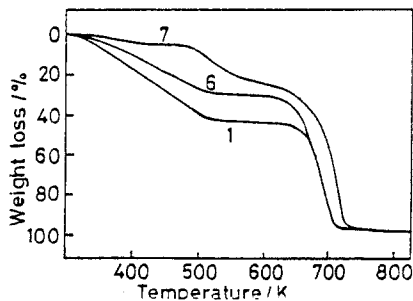

Fig. 3 TG curves of copolymers 1, 6 and 7. DMFwt%: 1, 42.9; 6, 30.0; 7, 0

(onset temperature) is attributed to decomposition of the ends of the network, because of the rapid decrease in mass, the loss amounting to about 10%, and the mass loss in the vicinity of the boiling point of MAA (436 K).

Figure 2 shows the effects of the BPO amount on the TG curves. The mass loss in the first stage of the TG curve of copolymer 5, which occurs around the boiling points of MAA and DMF, is due to the vaporization of unpolymerized MAA and
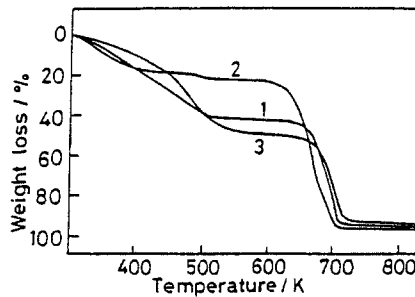
Fig. 4 TG curves of copolymers 1, 2 and 3. MAA/POTMDM/g/g: 3, 14.3/1.0; 1, 2.9/1.0; 2, 0.6/1.0

the polymerization solvent, DMF. The good fit of the TG curves between copoly-mers 1 and 4 suggests that most of the MAA is polymerized under these polymeri-zation conditions, and therefore 40% of the mass loss in the first stage is due to the vaporization of DMF and dehydration from PMAA.

Figures 3 and 4 show the dependence of the onset temperature of the last stage on the DMF concentration and the PMAA/POTM composition in the polymeriza-tion. This is more apparent from the values of the onset temperature of mass loss in the last stage, the DMF concentration and the MAA/POTMDM composition (Table 2).

Table 2 Dependence of decomposition temperature on DMF concentration and MAA/POTMDM composition

Polymer	On- or off-set temp./K			DMF conc./	MAA/POTMDM
	Stage 1	Stage 2	Stage 3	wt%	comp./g/g
PMAA	(430)	536	753	0	
PPOTMDM	(430)	–	702	0	
POTMG	–	–	614	0	
POTMDM	–	–	546	0	
copolymer 3	–	(513)	680	48.5	14.3/1.0
copolymer 7	403	500 (547)	680	0	2.9/1.0
copolymer 1	–	(510)	660	42.9	2.9/1.0
copolymer 4	–	(510)	660	42.4	2.9/1.0
copolymer 6	–	(521)	660	30.0	2.9/1.0
copolymer 5	(423)	–	648	42.9	2.9/1.0
copolymer 2	(395)	495 (513)	640	27.2	0.6/1.0

Numbers in parentheses are values of off-set temperature.

Differential scanning calorimetry

Only a single peak, due to the fusion of POTM, appears in the DSC curves of PMAA-*net*-POTM, because the temperature scan was stopped before the evolution of gas. Table 3 shows the peak temperature values relating to the fusion of POTM.

Table 3 DSC peak temperature and compositions of copolymers

Copolymer	Peak temp./ K	Composition/mol/mol		
		POTMDM/MAA	BPO/MAA	DMF/MAA
2	283	$4.9/10^2$	$1.0/10^3$	1.0/1.0
5	278	$9.9/10^3$	$1.0/10^4$	1.0/1.0
1	288	$9.9/10^3$	$1.0/10^3$	1.0/1.0
4	283	$9.9/10^3$	$1.0/10^2$	1.0/1.0
3	285	$2.0/10^3$	$1.0/10^3$	1.0/1.0
6	unknown	$9.9/10^3$	$1.0/10^3$	4.0/10
7	unknown	$9.9/10^3$	$1.0/10^3$	0/0

The effects of the DMF concentration and the MAA/POTMDM composition in the polymerization are unclear relative to the TG results. However, interesting results may be discerned. The peak temperature of copolymer 1 is higher than that of copolymer 4, in spite of there being no difference in TG curve between copolymers 1 and 4. The polymerization conditions for copolymer 1 are the same as those for copolymer 4, besides the BPO concentration. No peak appears in the DSC curve of copolymer 7, which is expected to be a polymer network with high heterogeneity. We attribute this to freezing of the POTM chains by frozen heterogeneous moieties.

Concluding remarks

This paper reports effects of the PMAA/POTMDM/BPO/DMF composition in the polymerization on the TG and DSC data for PMAA-*net*-POTM. Some significant conclusions may be mentioned:

1) The TG curves of PMAA-*net*-POTM are a mix of the TG curves of PMAA and POTMDM polymer. Mass loss occurs in the following stages: vaporization of DMF and unpolymerized MAA, decomposition of the ends of the networks, dehydration from PMAA, decomposition of POTM chains, and decomposition of PMAA anhydride.

2) The higher the DMF content of PMAA-*net*-POTM, the more unclear the stages of decomposition of the ends, the dehydration from PMAA, and the decomposition of the anhydride in the TG curves.

3) No peak due to melting of the POTM chain appears in the DSC curve of PMAA-*net*-POTM, which is expected to be a polymer network with high heterogeneity.

References

1 J. Bastide and L. Leibler, Macromolecules, 21 (1988) 2647.
2 E. Mendes, B. Girard, C. Picot, M. Buzier, F. Boue and J. Bastide, Macromolecules, 26 (1993) 6873.
3 M. Shibayama, H. Takahashi, H. Yamaguchi, S. Sakurai and S. Nomura, Polymer, 35 (1994) 2944.
4 H. Takahashi, M. Shibayama and S. Nomura, Macromolecules, 28 (1995) 5547.
5 J. Brandrup and E. H. Immergut, Ed., Polymer Handbook 2nd Ed., John Wiley & Sons, New York 1975, p. III–148.
6 Appears in the present paper.
7 T. Kojima, K. Masuda and K. Tago, J. Appl. Polym. Sci., 50 (1993) 2197.