# Thermoanalysis and Rheological Behavior of Emulsion Copolymers of Methyl Methacrylate, N-Phenylmaleimide and Styrene

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Terpolymers of methyl methacrylate (MMA), N-phenylmaleimide (PMI) and styrene (St) were synthesized by emulsion copolymerization. The thermal stabilities of terpolymers were studied by a programmed thermogravimetric analysis (TGA) technique. Terpolymers show a considerable increase in decomposition temperature with increasing feed content of PMI and St. The glass transition temperatures  $(T_g)$  of copolymers were measured by differential scanning calorimetry (DSC) and torsional braid analysis (TBA). The terpolymer's  $T_g$  increases markedly with the increasing PMI feed content, while it decreases with increasing St feed content. The rheological behaviors of copolymers were also studied. The terpolymer's apparent viscosity in melt decreases with increasing feed contents of PMI and St. The terpolymer's flow index *n* increases with the increasing feed content of PMI. The results also show that the difference value between  $T_{gDSC}$  and  $T_{gTBA}$ ,  $\Delta T_g$  increases with an increase in the terpolymer's flow index.  $\tilde{M}_w$  and  $\tilde{M}_n$  of copolymers were also determined by gel permeation chromatography (GPC).

# INTRODUCTION

The thermal stability of a polymer is an important aspect of its properties. There has been a considerable interest in the copolymers that contain maleimide moieties especially of N-phenylmaleimide (PMI) because of its noticing thermal property (1, 2). The polymer's heat resistance property showed an effective increase when it copolymerized with PMI. This is a valuable way to improve the polymer's thermal property.

PMI is a monomer with a structure of the 1,2-ethylenic type and a five-membered planar ring, which completely hinders the rotation of the imide residues around the backbone chain of the macromolecule. So the incorporation of PMI into polymer's backbone will lead to copolymers with great structural stiffness as well as a higher thermal stability.

For the present study methyl methacrylate (MMA) has been selected because of its wide use in the field of the modern plastics technology. The solution copolymerization of MMA with PMI has been studied previously (1). The copolymer's  $T_g$  increases almost linearly with increasing content of PMI. The studies of Hu

Xiaodong *et al.* showed that the copolymer's thermal stability increased further by the incorporation of styrene into the system (3). However, studies on the relationship between copolymer's rheological behavior, flow index and the feed contents of PMI, St have been lacking until now.

In solution copolymerization of PMI with other vinyl monomers, the desired copolymer structures and properties are difficult to control by simply adjusting the monomer's composition (4). In solution copolymerization of MMA with PMI, the two monomer reactivity ratios are different:  $r_{PMI} < 1$  and  $r_{MMA} > 1$ , so the copolymer has a tendency to contain more MMA than PMI. In this study, MMA-PMI-St copolymers were synthesized by emulsion copolymerization, and the relationships between the copolymer's average molecular weight, thermal property, glass transition temperature, flow index and monomer feed composition were investigated.

#### EXPERIMENTAL

#### Materials

MMA, St were washed twice with 5% solution of sodium hydroxide to eliminate inhibitor, and a few

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times with distilled water, then dried over anhydrous calcium sulfate. The synthesis of PMI was carried out in one stage according to the method developed by Matsunaga (5), then recrystallized twice from ethyl al-cohol-water (volume ratio: 1:2). The MMA, St, emulsifying agent sodium lauryl sulfate (SLS), initiator  $K_2S_2O_8$  and  $Al_2(SO_4)_3$  were all analytically pure and supplied by Beijing Chemical Regent Corporation. Distilled deionized water (DDW) was used in all experiments.

## **Emulsion Copolymerization**

The copolymerization was carried out in a dried, clear 100 ml four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. Monomer solution was added to a solution of SLS, then stirred over 15 minutes under nitrogen before partial  $K_2S_2O_8$  solution added to it. The system was then heated to  $80^{\circ}$ C. The residual  $K_2S_2O_8$  solution was added to the system 0.5 hour after the reaction. The copolymerization proceeded under nitrogen atmosphere at 80-85°C for about two hours, then was stopped and precipitated by  $2\% \text{ Al}_2(SO_4)_3$  solution. The copolymer was isolated by filtration, and washed a few times with hot water, dried, then washed with methyl alcohol in a flask within a rotating magnet in it for about 12 hours to remove the residual PMI monomer and SLS. The copolymer was then dried in a high vacuum drying oven. The conversion was measured gravimetrically and was always more than 90%. The composition of copolymer was measured by elemental analysis using a PE-240 elemental analyzer. Monomer feed proportions and the analysis results are summarized in Table 1. The results show that the copolymers' compositions were related to the monomer feed proportions.

## **Copolymer Analysis**

Samples were dried in a high vacuum drying oven at 60°C for 24 hr. Copolymer molecular weights were measured using a SN-01A gel permeation

Table 1. Emulsion Copolymerization of MMA, St and PMI<sup>a</sup>.

	Ingredients	Copolymer's	
MMA:PMI:St <sup>b</sup>	SLS°,g	K <sub>2</sub> S <sub>2</sub> O <sub>8,</sub> g	(MMA:PMI:St)
95:0:5	0.45	0.045	95.3:0:4.7
90:5:5	0.45	0.045	91.3:4.4:4.3
85:10:5	0.45	0.045	86.9:9.0:4.1
80:15:5	0.45	0.045	81.1:14.0:4.9
75:20:5	0.45	0.045	76.2:19.2:4.6
70:25:5	0.45	0.045	70.9:24.8:4.3
65:30:5	0.45	0.045	64.3:30.6:5.1
95:5:0	0.45	0.045	96.5:3.5:0
85:5:10	0.45	0.045	85.6:4.7:9.7
80:5:15	0.45	0.045	81.7:4.1:14.2
75:5:20	0.45	0.045	74.1:4.6:21.3
65:5:30	0.45	0.045	63.8:5.2:31.0

"Solid content is 30 wt%.

<sup>b</sup>Total monomer content is 15g.

°Sodium lauryl sulfate.





Fig. 1. FTIR spectra of copolymers. (a) MMA-St (95:5); (b) MMA-PMI-St (80:15:5); (c) MMA-PMI-St (65:30:5).

chromatography (GPC). Tetrahydrofuran was used as flow phase and flow rate was 1 ml/min. The column was calibrated by using commercially available narrow-distribution polystyrenes. Inherent viscosity was measured using an Ubbelohde viscometer and a 1.0g/ dL tetrahydrofuran solution at  $25^{\circ}$ C.

Thermogravimetric analysis was carried out by means of a Shimadzu DT-40 thermogravimeter (TG). Half-loss weight temperature  $T_{50}$  was obtained when the weight loss of the copolymer reach 50% at a heating rate of 10°C/min in air atmosphere.

The copolymer's  $T_{gDSC}$  was measured using a Shimadzu DT-40 differential scanning calorimetry (DSC) with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference material at a heating rate of 20°C/min under nitrogen.  $T_{gDSC}$  value was taken from the midpoint of the temperatures of the initial and final tangents in the DSC traces (6).

The glass transition temperature of the copolymer was also measured using a GDP-3 torsional braid analysis (TBA) at a heating rate of  $2^{\circ}C/min$ . T<sub>gTBA</sub> was taken from the maximum of logarithmic decrement in amplitude per cycle  $\Delta$ .

Shimadzu 301 Koka flow tester was used to test the copolymer's rheological property under temperature 200°C at different shearing stresses. The  $\dot{\gamma}_{\omega}$  was improved for non-Newtonian.

PMI Feed Content, wt%	0	5	10	15	20	25	30
M <sub>w</sub> 10 <sup>4</sup>	19.56 (0.23)	25.86 (0.68)	25.82 (0.94)	27.10 (0.37)	24.08 (0.20)	22.34 (0.4)	20.55 (0.25)
<b>M</b> _10 <sup>4</sup>	1.48 (0.31)	3.79 (0.15)	6.74 (0.50)	7.06 (0.34)	5.74 (0.28)	5.6 (0.42)	5.16 (0.34)
M <sub>w</sub> /M <sub>n</sub>	13.2 (1.5)	6.83 (0.52)	3.83 (0.30)	3.84 (0.14)	4.20 (0.33)	3.99 (0.20)	3.98 (0.36)

Table 2. Copolymer Molecular Weight at Different PMI Feed Content (St Feed Content 5 wt%).

\*The values in the brackets are standard deviations

Table 3. Copolymer Molecular Weight at Different St Feed Content (PMI Feed Content 5 wt%).

St Feed Content, wt%	0	5	10	15	20	30
 M <sub>w</sub> , 10 <sup>4</sup> M <sub>n</sub> , 10 <sup>4</sup>	11.33 (0.44) 1.21 (0.11)	25.86 (1.02) 3.79 (0.32)	26.73 (1.09) 3.71 (0.26)	21.11 (0.34) 3.60 (0.10)	18.27 (0.18) 3.56 (0.25)	17.93 (0.54) 2.89 (0.43)
$\widetilde{M}_{w}^{H}/\widetilde{M}_{n}$	9.36 (2.37)	6.83 (0.24)	7.21 (0.52)	5.86 (0.11)	5.13 (0.33)	6.21 (0.35)

## **RESULTS AND DISCUSSION**

Structure change in the copolymer was investigated by using a FTS-40 IR spectrophotometer. The IR spectra of MMA-PMI-St at different monomer feed proportions are shown in *Fig. 1*. With the incorporation of PMI, the most significant feature is the increase of the single substituted benzene group absorption (marked by an arrow). It is observed that the absorption peak of the single substituted benzene group gradually increases with inceasing PMI feed content. When no PMI has been fed, the absorption shows a small peak because of the existence of styrene segments. This indicates that the PMI content in the copolymer increased with increasing PMI feed content.

#### **Molecular Weight**

 $\overline{M}_{w}$  and  $\overline{M}_{n}$  of MMA-PMI-St emulsion copolymers at different PMI feed contents (St 5 wt%) and different St feed contents (PMI 5 wt%) are shown in *Table 2* and *Table 3*. As shown, both  $\overline{M}_{w}$  and  $\overline{M}_{n}$  increase with an increase of PMI and St content at low PMI (St) content, while having a peak and lower  $\overline{M}_{w}/\overline{M}_{n}$  under proper feed content of PMI and St.

Previous studies showed that there was a maximum copolymerization rate at  $f_{\text{St}}$  (styrene monomer mol fraction)  $\approx 0.3$  in solution copolymerization of St with

PMI because of the nearly alternating copolymerization behavior and the existence of charge-transfer complex (CTC) (7). The molecular weight model of St-PMI solution copolymer, which also showed a maximum value at proper St/PMI ratio, has also been obtained (8).

As known, polymerization reactions mainly take place in micelles in emulsion polymerization, and only one active radical can be tolerated in it, so the micelle will contain either one or zero radicals at any one time. The rate of the "on-off switching" is controlled by both the rate of radical production and the number of micelles in the reaction medium. So for a fixed initiator concentration and temperature the chain length, thus, the molecular weight of the polymer is a function of the rate of radical propagation  $\nu_{\rm p}$ , and not affected by other variables (9). And  $\nu_{\rm p}$  is a function of monomer feed ratio if the reactivity ratios are fixed, as reported, it will be a maximum at proper monomer ratio. So the molecular weight of copolymer was mainly affected by the monomer feed composition when copolymerization temperature, emulsifying agent and initiator concentrations are fixed, and should be a maximum at proper monomer ratio. This is the reason that the average molecular weight of MMA-PMI-St emulsion terpolymers varies at different PMI and St contents.

Table 4. Thermogravimetric Analysis Results of Copolymers at Different PMI Feed Content.

PMI Feed Content, wt%	PMMA	0	5	10	15	20	25	30
T <sub>i</sub> ,°C	262.4	266.8	280.9	291.3	301.3	301.8	307.8	307.4
T <sub>50</sub> ,°C	316.6	334.6	337.9	342.5	348.1	355.9	360.6	367.4

 Table 5. Thermogravimetric Analysis Results of Copolymers at Different St Feed Content

St Feed Content, wt%	0	5	10	15	20	30
T <sub>i</sub> , °C	283.4	280.9	282.6	280.8	280.6	283.4
T <sub>50</sub> , °C	327.0	337.9	338.1	339.6	339.1	339.0

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Fig. 2. Thermogravimetric analysis diagrams (10°C/min). (a) PMMA; (b) MMA-St (95:5); (c) MMA-PMI-St (90:5:5); (d) MMA-PMI-St (65:30:5).



Fig. 3. Effect of PMI feed content on terpolymer  $T_a$ .



Fig. 4. Effect of St feed content on terpolymer  $T_q$ .



Fig. 5. Terpolymer viscosity at different PMI feed content.

## **Thermogravimetric Aanalysis**

The thermal stability of the copolymer has been arbitrarily defined as a function of the initial thermal stability temperature  $(T_i)$  and the half weight loss temperature  $(T_{50})$  at particular environmental conditions described previously. Experimental results are given in *Tables 4–5*. For comparison, some thermograms on the studied series of copolymers are shown in *Fig. 2*.

Many studies show that PMMA decomposes at high temperature.  $T_{50}$  of PMMA was obtained to be 316.6°C in our study. The results in *Tables 4–5* indicate that thermal stability tends to increase as both the PMI and St feed contents increase. Copolymer  $T_i$  and  $T_{50}$ both increased with the increasing PMI feed content. But with the increasing feed content of St, copolymer  $T_i$  has not been improved and  $T_{50}$  increased only when the St feed content was below 5 wt%.  $T_{50}$  increased 18°C when PMMA copolymerized with 5 wt% St, but  $T_i$  only increasd 4.4°C.  $T_{50}$  of MMA-PMI-St (65:30:5) is 50.8°C higher than neat PMMA, and  $T_i$  is 45°C higher than PMMA because of the presence of 1,2-ethylenic units directly linked to styrene units (1). With 5 wt% PMI incorporation, polymer's  $T_{50}$  increased to 327.0°C with 10.4°C increased and  $T_i$  increased 21°C. The results are related to the previous studies of solution copolymerization of MMA-PMI-St (3). Thus, the incorporation of PMI and St to MMA in emulsion copolymerization will highly restrain the decomposition reaction of PMMA.

## **Glass Transition Temperature**

Copolymer  $T_g$  was another important indication of its thermal property. Copolymer  $T_g$  determined by DSC and TBA are shown in *Figs.* 3–4. The results



Fig. 6. Terpolymer viscosity at different St feed content.

show that  $T_a$  increases with increasing PMI feed content and decreases with increasing St feed content although there are differences between DSC and TBA results.

An interesting fact can be found from Figs. 3-4: obviously, the  $T_{\text{gTBA}}$  is higher than  $T_{\text{gDSC}}$  for the same sample. This is due to the different test frequencies of the two different locating Tg methods. As known, the test frequency of DSC, a static method is about 10-3 Hz, which is much lower than 0.5 Hz, the test frequency of TBA, a dynamic method (10).

# **Rheological Behavior**

Terpolymer apparent viscosities at different shear rates are shown in Fig. 5 and Fig. 6, respectively. As is shown in the Figures, terpolymer  $\eta_a$  decreases with increasing shear rate, exhibit a behavior of pseudoplastic flow in melt.

Flow index n and  $\ln K$  of Ostwald-De Waele equation,  $\eta_a = K\dot{\gamma}^{n-1}$ , of copolymers are calculated and shown in Table 6-7. At the same time,  $\ln(K/(10^{-4} M_{u})^{3.4})$  was



Fig. 7.  $\Delta T_g$  versus terpolymer flow Index n of different PMI feed content.

calculated to investigate the effect of molecular structure on copolymer viscosity by assuming  $\eta_a \propto M_w^{3.4}$  to eliminate the influnce of difference of copolymer molecular weight.

Figures 5-6, Tables 6-7 show that copolymer apparent viscosity  $\eta_a$  decreases with an increase of both PMI and St feed content.  $\ln(K/(10^{-4} M_{\mu})^{3.4})$  decreased rapidly when PMI and St were incorporated but does not decrease with a further increase of PMI and St feed content. This is mainly because of the lower polarities of PMI and St segments that minimize the intermolecular forces in the polymers. At the same time we can find the copolymer flow index n increases largely with the increasing PMI feed content because of PMI's five-membered structure's hindering the rotation of the macromolecule and increasing the chain's stiffness.

We can also find the difference value  $\Delta T_q$  between  $T_{\text{gTBA}}$  and  $T_{\text{gDSC}}$  of copolymers was not a constant in Fig. 3.  $\Delta T_a$  increases with the increasing PMI feed content. The plot of  $\Delta T_q$  versus flow index n of copolymers

Table 6. Effect of PMI Feed Content on Terpolymer Viscosity.										
0	5	10	15	20	25	30				
.30 .36 .25	0.32 13.26 2.20	0.36 12.87 1.82	0.40 12.84 1.62	0.45 12.58 1.76	0.54 12.20 1.64	0.63 11.80 1.29				
	.30 .36 .25	<b>5</b> .30 0.32 .36 13.26 .25 2.20	5         10           .30         0.32         0.36           .36         13.26         12.87           .25         2.20         1.82	5         10         15           .30         0.32         0.36         0.40           .36         13.26         12.87         12.84           .25         2.20         1.82         1.62	5         10         15         20           .30         0.32         0.36         0.40         0.45           .36         13.26         12.87         12.84         12.58           .25         2.20         1.82         1.62         1.76	5         10         15         20         25           .30         0.32         0.36         0.40         0.45         0.54           .36         13.26         12.87         12.84         12.58         12.20           .25         2.20         1.82         1.62         1.76         1.64				

Table 7. Effect of St Feed Content on Terpolymer Viscosity.

St Feed Content, wt%	0	5	10	15	20	30
Flow Index	0.32	0.32	0.32	0.32	0.36	0.37
InK	13.36	13.26	13.01	12.96	12.77	12.29
in(K/(10 <sup>-4</sup> M <sub>w</sub> ) <sup>3.4</sup> )	5.11	2.20	1.84	2.59	2.89	2.48

at different PMI feed content is given in Fig. 7. Obviously, with higher flow index *n*, a higher  $\Delta T_g$  value will be observed.

# CONCLUSIONS

- 1. The incorporation of PMI and St to PMMA in emulsion copolymerization will highly restrain the thermal decomposition reaction of PMMA. PMI is an effective monomer for improving the thermal properties of materials, especially for glass transition temperature and decomposition temperature.
- 2. Terpolymer's flow property will improve by the incorporation of PMI and St segments. And terpolymer's flow index *n* increases with the increasing feed content of PMI.
- 3. Combined with static and dynamic method is more effective way to reflecting the movement of molecular chain and stiffness for MMA-PMI-St terpolymer.
- 4. The difference between  $T_g$  obtained by DSC and TBA not only related to the test frequency but also affected by the polymer's flow index. Higher flow index, higher  $T_{gTBA}$ - $T_{gDSC}$  value will be observed.

# ACKNOWLEDGMENT

This paper is the result of a project supported by Natural Science Foundation of Hebei Province.

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