

Free-Radical Copolymerization and Kinetic Treatment of Methyl Methacrylate with *N-P*-Tolylmaleimide

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ABSTRACT: The free-radical copolymerization of methyl methacrylate (MMA) with *N-P*-tolylmaleimide (NPTMI) at 77°C in cyclohexanone solution initiated by AIBN was studied. The copolymer composition was calculated from the nitrogen content estimated by the Mico-Kijedldahl's method and by elemental analysis. The reactivity ratios have been calculated by Fineman and Ross method. The monomer reactivity ratios were $r_{\text{NPTMI}} = 1.24$, $r_{\text{MMA}} = 2.1$. The glass transition temperature (T_g) of the copolymers were determined by torsion braid analysis (TBA). The thermal stability

was determined by thermogravimetric analysis (TGA). T_{50} , temperature at which the weight loss reaches 50%, was abstained. The results showed that the M_n and M_w increased, whereas the NPTMI feed content increased. The T_g and T_{50} increased dramatically. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 867–870, 2004

Key words: *N-P*-tolylmaleimide; methyl methacrylate; kinetics; radical polymerization; thermal properties

INTRODUCTION

N-substituted maleimides have become interesting monomers, which can be either radically copolymerized with other vinyl monomers^{1–2} or homopolymerized^{3–8} by way of radical or anionic polymerization despite their 1,2-disubstituted ethylene structure. Numerous works on their radical polymerization and copolymerization have been performed so far because of the superiority of their polymers or copolymers in thermal stability.^{9,10} Literature^{11,12} reported that a few of these monomers have been used to treat the kinetic data of systems with the anticipated participation of a charge-transfer complex (CTC) in the copolymerization process.

Some reports on the synthesis of copolymers of MMA with *N*-(alkyl-substituted phenyl)maleimides (RPhMI) and their thermal behavior are available.¹³ When the maleimide unit, which has a rigid structure, is introduced into a flexible vinyl polymer chain, the intra- and intermolecular interactions, which differ from those of homopolymer, are expected to play an important role in the properties of the copolymer. Patel¹⁴ has calculated the reactivity ratios of the *N-P*-tolylmaleimide (NPTMI) and methyl acrylate (MA) in different methods. However, the properties of the copolymer of the NPTMI and MA have not been reported until now. In this article, NPTMI was selected

to copolymerize with methyl methacrylate (MMA), a widely used monomer in the field of modern plastic technology. The reactivity ratios of monomers and the effects of the monomer feed composition on the properties of the copolymer such as the average molecular weight (M_n and M_w), glass transition temperature (T_g), and degradation temperature were investigated.

EXPERIMENTAL

Materials

NPTMI is prepared from the reaction of maleic anhydride and *P*-toluidine in one stage according to the methods described in the literature.¹⁵ The product was recrystallized from a mixture of ethanol and water (1 : 1.8). After recrystallization, NPTMI gave yellow needles with a melting point (mp) of 154°C, consistent with the literature.¹³ Cyclohexanone and MMA were supplied by Beijing Chemicals Co., Ltd. (Beijing City, China). Cyclohexanone was distilled before use. MMA was washed with aqueous sodium hydroxide to remove the inhibitor, then washed again with water to neutralize, and then distilled before use. The water used in all experiments was distilled and deionized water (DDW) (Beijing Chemicals Co., Beijing, China).

AIBN (Tianjin Chemical Reagent Co., Tianjin, China) was purified by crystallization from methanol three times.

POLYMERIZATION PROCEDURE

The free-radical solution copolymerization method was adopted for the synthesis of copolymers of differ-

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TABLE I
Experimental Data for the Copolymer PM [NPTMI(M_1) copolymerized with MMA(M_2)]

Copolymer	PM-1	PM-2	PM-3	PM-4	PM-5	PM-6
Feed monomers by weight	1 : 9	2 : 8	3 : 7	4 : 6	5 : 5	6 : 4
Mole fraction of NPTMI in the monomer feed (f_1)	0.05	0.121	0.186	0.259	0.351	0.444
Conversion (%)	14.8	18	19.9	18.2	20.5	19.1
N in the copolymer (wt %)	0.347	0.967	1.456	2.18	2.742	3.393
Mole fraction of NPTMI in the copolymer from % N	0.025	0.073	0.114	0.18	0.234	0.307

Solvent: cyclohexanone; reaction time: 10 min; initiator: AIBN; reaction temperature: 77°C.

ent compositions. The accurately weighed NPTMI, MMA, and AIBN were placed in clean glass vessels, flushed with nitrogen several times to sweep oxygen, and then sealed off. The copolymerization was carried out in a water bath at 77°C under stirring. The glass tube was removed after an appropriate time interval, and the copolymerization was stopped by decreasing the temperature immediately. Then the contents were poured out and precipitated. The sediment was reprecipitated and dried under vacuum. The gravimetric weight conversion of MMA/NPTMI copolymerization was obtained.

COPOLYMER ANALYSIS

The composition of copolymer was calculated on the basis of the nitrogen content in the copolymer measured by a PE-240 elemental analyzer.

The M_n and M_w of the copolymer were determined by using a P200 gel permeation chromatography (GPC). Tetrahydrofuran was used as the flowing phase and the flow rate was 1.00 mL/min. The column was calibrated by using commercially available narrow distributed polystyrene.

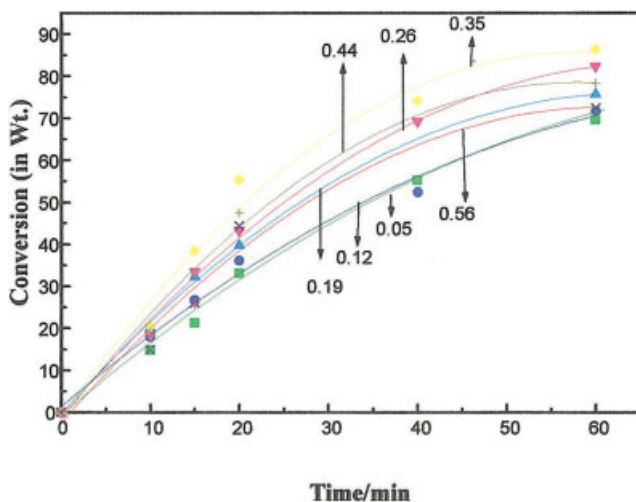


Figure 1 Relationship between molar conversion and reaction time.

The thermal stability of the copolymers was characterized by thermogravimetric analysis (TGA). The experiment was carried out on a Shimadzu DT-40 thermogravimetric analyzer at a heating rate of 10°C/min in an air static atmosphere.

The glass transition temperatures (T_g 's) of the copolymer were measured by torsional braid analysis (TBA). The experiments were performed on a GDP-3 TBA unit at a heating rate of 2°C/min. The T_g was taken from the maximum of logarithmic decrement in amplitude per cycle (Δ).

RESULTS AND DISCUSSION

Kinetics of MMA/PMI copolymerization in cyclohexanone

The free-radical copolymerization of PMI (M_1) with MMA (M_2) was performed in cyclohexanone by using AIBN as initiator. The copolymer compositions were calculated on the basis of the nitrogen content in the copolymers measured by an elemental analyzer. The polymerization conditions and the copolymer compositions were shown in Table I. The effect of the initial molar fraction f_1 on the molar conversion in weight

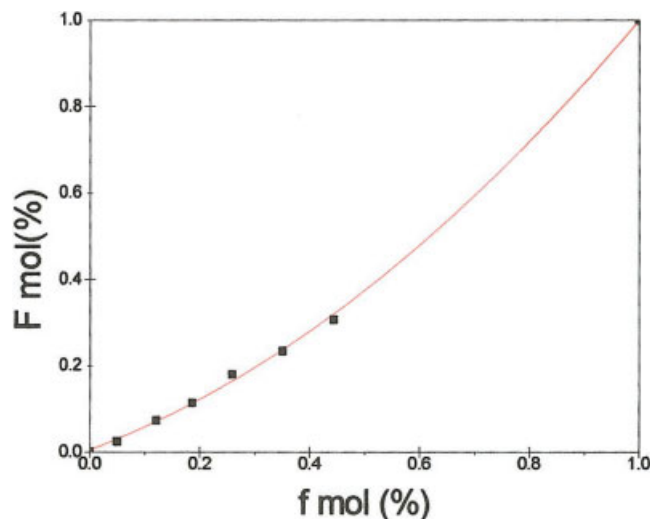


Figure 2 f_1 - F_1 curve for NPTMI/MMA copolymerization.

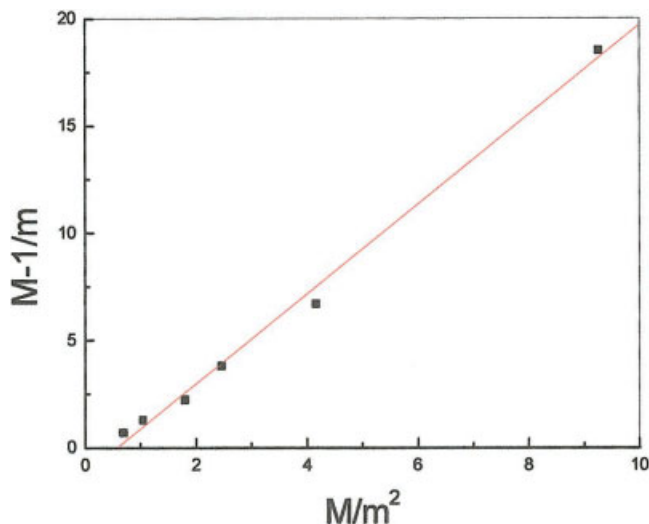


Figure 3 Relationship between $(1M)/m$ and M/m^2 .

versus time in PMI/MMA copolymerization at 77°C in cyclohexanone was shown in Figure 1. The relationship between f_1 , the initial molar fractions of imide in the monomer feed, and F_1 , the molar fractions of imide in the copolymers, is shown in Figure 2. As can be seen in Figure 1, when $f_1 = 0.3$, the initial copolymerization rate has a peak value. The monomer reactivity ratios $r_1 = 1.24$ and $r_2 = 2.1$ were calculated by using Fineman and Ross (FR)¹⁶ methods (Fig. 3 and Table II). This fact means that NPTMI is less active than MMA in this copolymerization system.

Average molecular weight

The average molecular weights of copolymers at different NPTMI feed contents are presented in Table III. Both the \bar{M}_n and the \bar{M}_w increased with increasing NPTMI content.

Thermogravimetric analysis

For the purpose of comparison, TGA curves were shown in Figure 4. The temperature of the initial thermal degradation (T_{init}), the temperature of 50% weight loss (T_{50}), and the residual weight at 500°C are summarized in Table IV. The results showed that the T_{init} , T_{50} , and the residual weight at 500°C increased with increasing f_1 and all of the copolymers exhibited a

TABLE II
 $M - 1/m$ and M/m^2 for the Copolymer

Copolymer	PM-1	PM-2	PM-3	PM-4	PM-5	PM-6
$M-1/m$	18.51	6.69	3.81	2.23	1.28	0.70
M/m^2	9.26	4.16	2.46	1.80	1.04	0.69

$M = F_1/F_2; m = f_1/f_2.$

TABLE III
Experimental Data for the Copolymer [NPTMI copolymerized with MMA]

Copolymer	Feed monomers		$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$	\bar{M}_w/\bar{M}_n
	by weight				
PM-1	1 : 9		1.24	3.06	2.47
PM-2	2 : 8		1.36	3.36	2.48
PM-4	4 : 6		1.85	3.96	2.13
PM-5	5 : 5		1.53	4.91	3.19
PM-6	6 : 4		2.11	6.47	3.07
PM-7	7 : 3		3.27	8.06	2.46

Solvent: cyclohexanone; reaction time: 15 min; initiator: AIBN; reaction temperature: 77°C.

higher T_{50} than neat PMMA, which means that all copolymers had a better thermal stability than PMMA. The T_{50} of PMMA was 569 K and that of the copolymer was 616.9 K when NPTMI feed content was 20%, 47.9 K higher than that of neat PMMA. This is because the incorporated five-member planar cyclic structure in the chain of copolymer enhances the thermal stability of the copolymer.¹⁷

Glass transition temperature

The T_g 's of the copolymers are considerably higher than the value of 378.4 K for PMMA itself, as can be seen from Table V. At a level of NPTMI incorporation of as low as 1 wt %, the T_g was 12 K higher than that of neat PMMA. Table V also shows that T_g of the copolymer obviously increases with an increase in the content of feed NPTMI in this system. This is due to

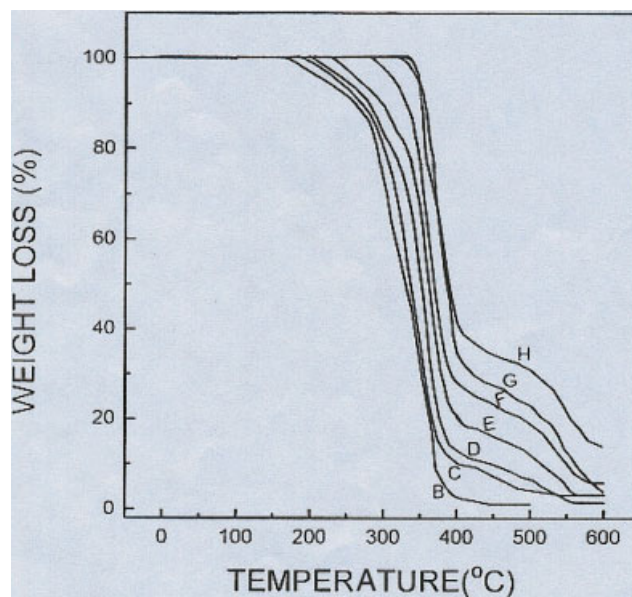


Figure 4 TGA curves of copolymers, NPTMI feed content (% in wt). B: 10%; C: 20%; D: 30%; E: 40%; F: 50%; G: 60%; H: 70%.

the bulky NPTMI units incorporated into the polymer chain that can significantly block the rotation of the chain segments. Therefore, NPTMI can improve greatly the thermal resistance of poly(methyl methacrylate) (PMMA).

CONCLUSION

In this investigation, MMA was copolymerized with NPTMI by using free-radical initiators. The conversion was limited to about 10%. A wide range of initial monomer feed ratios was chosen.

The reactivity ratios for both systems have been evaluated by using FR. Since reactivity ratios indicate the distribution of monomer units in a polymer chain, this can aid in choosing the desired composition of copolymers of specific end-use requirements.

In this article, it can be seen that NPTMI is a valuable monomer able to improve the thermal properties of PMMA. The glass transition temperature and deg-

TABLE IV
Results of Thermogravimetric Analysis

Copolymer	T_{init} (°C)	T_{50} (°C)	Residue at 500°C (%)
PM-1	276.47	329.43	2.96
PM-2	297.25	343.89	4.39
PM-3	302.14	355.30	7.81
PM-4	311.91	361.61	12.83
PM-5	327.80	369.76	18.96
PM-6	340.84	384.22	22.23
PM-7	345.51	459.78	45.72

Solvent: cyclohexanone; reaction time: 15 min; initiator: AIBN; reaction temperature: 77°C.

TABLE V
 T_g of Copolymers

Copolymer	PM-1	PM-2	PM-5	PM-6	PM-7
Feed monomers by weight	1 : 9	2 : 8	5 : 5	6 : 4	7 : 3
T_g (K)	390.5	405.7	411.5	422.8	443.3

Solvent: cyclohexanone; reaction time: 15 min; initiator: AIBN; reaction temperature: 77°C.

radation temperatures of the copolymer are greatly enhanced by the incorporation of NPTMI.

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