

Synthesis and Characterization of Terpolymer of *N*-Cyclohexylmaleimide, Methyl Methacrylate, and Acrylonitrile

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ABSTRACT: Terpolymers of *N*-cyclohexylmaleimide, methyl methacrylate, and acrylonitrile (AN) at different AN feed content were synthesized by suspension polymerization. The thermal properties of the terpolymers such as glass transition temperature (T_g) and Vicat softening temperature (T_{Vicat}) were determined by torsion braid analysis and Vicat softening temperature tester, respectively. The value of T_g and T_{Vicat} decreased with increasing AN feed content. Thermogravimetric analyses were carried out with the results that the incorporated AN units enhanced the thermal stability of the resulting polymers and a second degradation step appeared with the addition of AN. The mechanical proper-

ties (tensile strength and impact strength) of the terpolymers were also detected and the results show that the tensile strength and impact strength of terpolymers increase with increasing AN feed content. The rheological results illustrated that the terpolymers showed rheological behavior similar to that of pseudoplastic liquid. The apparent shear viscosity decreased with the increasing of AN feed content. The flow power index n increased with increasing AN feed content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 792–796, 2007

Key words: *N*-cyclohexylmaleimide; methyl methacrylate; acrylonitrile; structure; properties

INTRODUCTION

In recent years, particular attention has been paid to the copolymerization of *N*-substituted maleimide with vinyl monomers such as methyl methacrylate (MMA), styrene (St), because of their interesting polymerization behavior and the superior thermal properties of the resulting copolymers.^{1–4} It has been experimentally and theoretically⁵ proven that the incorporated *N*-substituted maleimide unit can effectively enhance both the glass transition temperature (T_g) and the thermal degradation temperature of these copolymers. While increasing T_g , however, the higher backbone rigidity also inevitably causes the decrease of the mechanical properties such as tensile strength and impact strength.⁶

Poly(methyl methacrylate) (PMMA) is the most popular commercial polymer in the acrylic industry used for glazing and optical application because of its excellent properties such as colorlessness, high light transmittance, weather resistance, light weight, and dimensional stability. However, PMMA has a poor heat resistance and the glass transition temperature (T_g) of conventional PMMA is generally between 85 and

105°C that is unsatisfactorily low. Recently, the copolymerization of *N*-cyclohexylmaleimide (ChMI) and MMA has been known as one of the best ways to improve the heat resistance of PMMA.^{7–11} The incorporation of rigid polar maleimide structure in the macromolecular chain increase both the T_g and the degradation temperature of the modified PMMA. Although ChMI is the best monomer to improve the thermal properties of PMMA, the coloration of these copolymers at high temperature has been pointed as an undesirable characteristic because of the monomeric ChMI and the unreacted ChMI monomer in the resin. Several attempts have been made to solve the problem. Yuichi et al.¹² tried to obtain the colorless poly(ChMI-MMA) by purifying the ChMI monomer. Their work showed that the ChMI contaminated with less than 0.9 wt % of *N*-cyclohexylaminosuccinic anhydride could be used for heat-resistant PMMA free from coloration. According to monomer reactivity ratio of MMA/ChMI in free radical copolymerization ($r_{MMA} = 1.35$, $r_{ChMI} = 0.24$),¹³ the monomer composition would drift with the running of the polymerization and chains of varying compositions would be formed. As a result, the copolymer of MMA and ChMI with homogeneous structure cannot be obtained by usual radical polymerization methods like suspension polymerization. According to Du et al.'s work,¹⁴ AN has a great influence on the polymerization behavior

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of reaction system containing N-substituted maleimide, and a homogeneous polymer can be obtained by suspension polymerization. For the particular reaction system of poly(ChMI-MMA), the effects of AN feed content on the properties of this polymer, such as thermal properties, mechanical properties, and the rheological behavior, were unavailable until now. In this work, terpolymers of MMA, ChMI, and AN were synthesized by suspension polymerization method, and the thermal properties, mechanical properties, and rheological properties were evaluated.

EXPERIMENTAL

Material

N-cyclohexylmaleimide (ChMI) provided by Zhuozhou Haihui Chemicals (Hebei Province, People's Republic of China) as commercial product and was recrystallized from a mixture of alcohol and water and stored in absence of light before use. MMA, AN, poly(vinyl alcohol) (PVA1788), and benzoyl peroxide (BPO) were supplied by Beijing Chemical Reagent (Beijing, People's Republic of China). MMA and AN were washed with aqueous sodium hydroxide to remove the inhibitor, then with water to neutrality. Poly(vinyl alcohol) (PVA1788) was used as suspending agent and served as supplied. BPO was used as initiator and purified by recrystallization in chloroform/methanol and dried under vacuum before use. The water used in all experiments was distilled and deionized water (DDW).

Synthesis of terpolymers

The polymerization of MMA, ChMI, and AN was carried out in a three-necked flask equipped with a reflux condenser, a stirrer, and a thermometer. The solution of ChMI and BPO in MMA and AN was charged into 300 mL solution of PVA in flask at 80°C under vigorous stirring. The recipes of polymerization were shown in Table I. After 4 h, the

temperature was raised to 100°C for an additional 2 h. The product was purified by washing with hot water, then dried in vacuum oven at 80°C for 6 h. The overall percentage conversion was over 95%.

Analysis method

The FTIR analysis was conducted on an FTS-40 IR spectrophotometer (Perkin-Elmer) and the elemental analysis of nitrogen, hydrogen, and carbon was performed on a PE-240 elemental analysis test apparatus (Perkin-Elmer, USA).

The \bar{M}_n and \bar{M}_w of the terpolymers were determined using a P200 gel permeation chromatography (GPC, Longzida, Beijing, People's Republic of China). 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.

The thermal stability of the polymers was characterized by thermogravimetric analyzer (TGA). The experiments were carried out on a Shimadzu DT-40 thermogravimetric analyzer (Shimadzu, Japan) at a heating rate of 10°C/min in an air atmosphere.

The dynamic mechanical properties of the terpolymers were measured by torsional braid analysis (TBA) from which $\tan \delta$ curves were obtained. The experiments were performed on a GDP-3 TBA unit (Changchun Intelligent Instrument and Equipment, People's Republic of China) at a heating rate of 2°C/min. The T_g was defined as the temperature at which the $\tan \delta$ passed through a maximum.

The T_{Vicat} values of the terpolymers were determined at a heating rate of 2°C/min. The temperature at which the needle, with a load of 1 kg, was pushed 1 mm into the sample was taken as T_{Vicat} . The experiments were carried on a KWK-300 Vicat softening temperature taster (Changchun Intelligent Instrument and Equipment, People's Republic of China).

The rheological behaviors of the terpolymers were investigated by a Shimadzu Koka flow test apparatus (Shimadzu, Japan). The temperature was fixed at

TABLE I
Suspension Polymerization^a of MMA, ChMI, and AN

Sample No.	Feed monomers (in wt %)			Terpolymer composition ^b (in wt %)			\bar{M}_n ($\times 10^4$)	\bar{M}_w ($\times 10^5$)
	MMA	ChMI	AN	MMA	ChMI	AN		
1	80	20	0	84.5	15.5	0	7.84	11.2
2	75	20	5	79.6	16.3	4.1	5.75	5.90
3	70	20	10	74.3	16.8	8.9	6.01	5.31
4	65	20	15	68.2	17.0	14.8	6.91	5.37
5	60	20	20	56.8	25.8	17.4	7.94	6.71
6	55	20	25	51.0	26.3	22.7	8.54	10.04

^a Solid content is 30%, PVA content 0.02% of the monomer, initiator content is 0.2% of the monomer.

^b Calculated from elemental results.

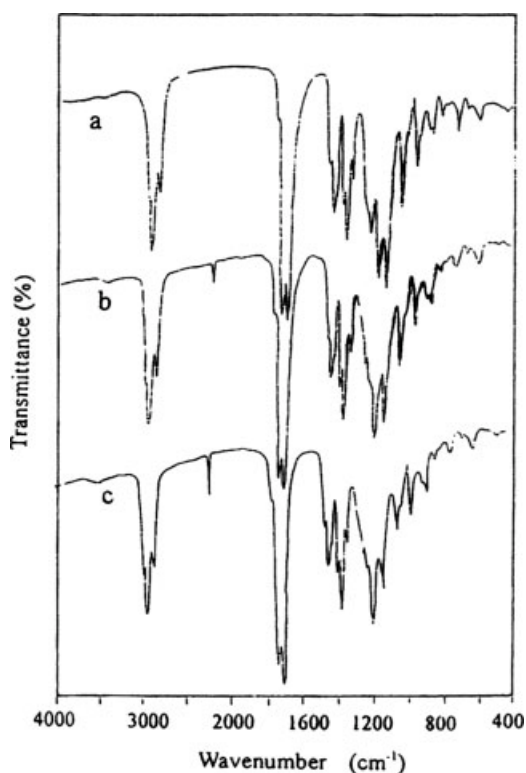


Figure 1 FTIR spectra of polymers: (a) MMA : ChMI = 80 : 20; (b) MMA : ChMI : AN = 65 : 20 : 15; (c) MMA : ChMI : AN = 55 : 20 : 25.

190°C. The nozzle diameter was 1 mm and the nozzle length was 10 mm. The weight of the test specimen was 1.0 g.

The samples used to determine mechanical properties were $100 \times 10 \times 5 \text{ mm}^3$ in size. The tensile strength (stress at yield) was measured at 25°C by using a WSM-10KB electronic tensile tester (Changchun Intelligent Instrument and Equipment, People's Republic of China) at a tensile rate of 10 mm/min. The sample number was 4 for each specimen. The notch impact strength was carried out on an X CJ-40 impact tester (Chengde Puhui, People's Republic of China) under the same conditions. The sample number was 6 for each specimen.

RESULTS AND DISCUSSION

Composition and structure

The IR spectra of the terpolymers with different monomer mixture proportion are shown in Figure 1. The absorption at 1710 cm^{-1} is attributed to C=O stretching frequency in ChMI, and the peak at 1728 cm^{-1} is the absorption of C=O in MMA. The sharp absorption at 2247 cm^{-1} assigned to the $-\text{CN}$ in AN show the existence of AN in the polymer. As seen from Figure 1, the peak at 1710 cm^{-1} increases

with increasing of AN feed content, which suggests that the ChMI conversion increase with the increasing of AN feed content. This result was proofed by the elemental analysis results as shown in Table I. As seen from the compositions of the terpolymers (Table I), the conversion of ChMI is lower in the ChMI/MMA suspension polymerization than that of terpolymer of ChMI/MMA/AN. When AN is introduced to the reaction system, the ChMI content is found to increase with increasing AN feed content, suggesting that the AN makes ChMI to react easily.

The molecular weights at different AN feed content were summarized in Table I. As seen from Table I, The molecular weights (\bar{M}_n , \bar{M}_w) of terpolymers was lower than that of ChMI-MMA copolymer and was increasing with increasing AN feed content in the study range of 5–25% AN feed content. The molecular weight distribution (\bar{M}_w , \bar{M}_n) of terpolymers at 0, 5, 10, 15, 20, and 25% AN feed content are 14.3, 10.3, 8.8, 7.8, 8.4, and 11.8, respectively. The large polydispersity of the samples is due to the suspension method and the lower reactivity of ChMI.

Thermal properties

TBA technique was employed to detect the T_g s of the samples and the results were shown in Figure 2. T_g and T_{Vicat} of polymers were shown in Figure 3. T_g of PMMA synthesized under the same condition is 105.4°C. TBA curves of all samples have a single peak, suggesting that the chain segment has a homogenous structure. All the terpolymers exhibit a higher T_g than pure PMMA, but it decreases with increasing of AN feed content. The linear relationship between T_g and AN feed content is expressed as follows:

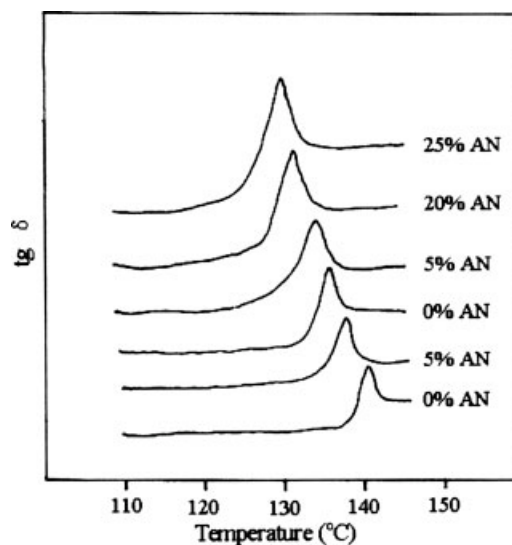


Figure 2 TBA curves of terpolymers at different AN feed content.

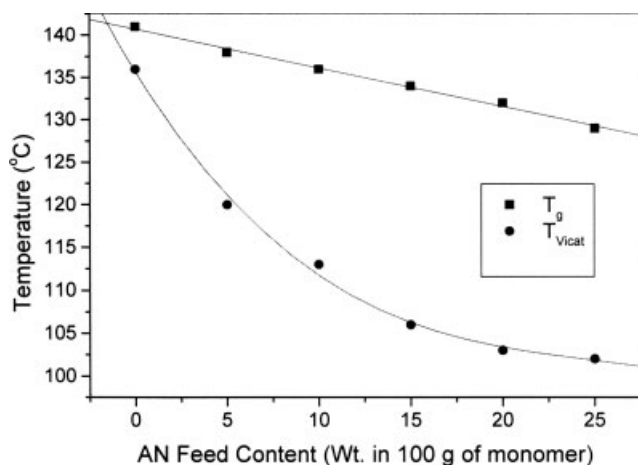


Figure 3 T_g and T_{Vicat} of terpolymers at different AN feed content.

$$T_g(^{\circ}\text{C}) = 140.56 - 47.4f_{AN}$$

where the f_{AN} is the feed content of AN in weight percent. The T_g value is thus decreased 0.474°C by per 1 wt % of AN.

T_{Vicat} of polymers is also decreased with AN feed content but it is not linear. T_{Vicat} of pure PMMA synthesized at same condition is 118°C . The T_{Vicat} of terpolymers at 0, 5, 10, 15, 20, and 25% of AN feed content is 136, 120, 113, 106, 103, and 102°C , respectively. Both T_g and T_{Vicat} indicate the chain segments' ability to move. The ChMI units incorporation in macromolecular chain greatly enhance the T_g and T_{Vicat} of PMMA for the bulky maleimide structure and cyclohexyl side group hamper the rotation of the chain segments seriously. The $-\text{CN}$ group has a dual role in the polymer chains. The higher polarity of $-\text{CN}$ can increase the interaction between the macromolecular chains, which increase the T_g , and on the other hand, the small bulk of AN reduce the stiffness of the chain, which decrease the

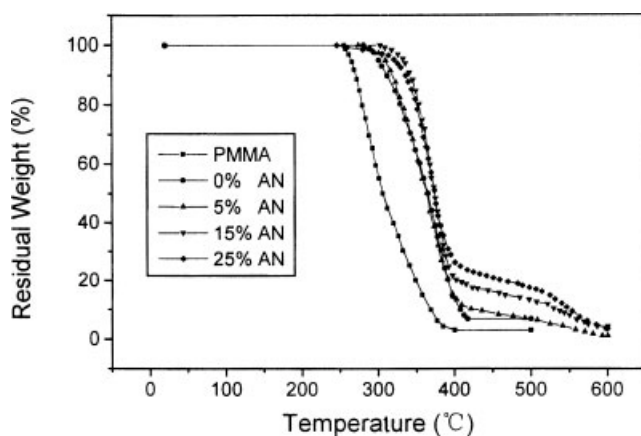


Figure 4 TGA curves of polymers.

TABLE II
Thermal Stability of the Terpolymers

AN feed content (%)	T_{d10} ($^{\circ}\text{C}$)	W_{500} (%)
0	302.7	9.58
5	319.1	6.17
10	321.2	9.42
15	341.8	13.33
20	336.9	12.17
25	335.4	17.76

value of T_g and T_{Vicat} . Seeing from the results, the bulk effect of AN is greater than its polarity effect.

Figure 4 shows the TGA curves of copolymer and terpolymers. The result for PMMA is also included as a comparison. Temperatures of 10% weight loss (T_{d10}) and the residual at 500°C (W_{500}) are listed in Table II. The results show that all the terpolymers have a higher T_{d10} than PMMA ($T_{d10} = 271.6^{\circ}\text{C}$), which means that AN improves the thermal stability of the polymers. Seeing from Figure 4, it is found that the thermal degradation of PMMA and poly(MMA-co-ChMI) proceeded via a single-step reaction and poly(MMA-co-ChMI) has a higher degradation temperature behavior. All terpolymers degrade via a two-step process, and a plateau appeared at about 400°C . This is caused by the incorporated AN, since the residual weight at the plateau increases with increasing AN feed content. This may result from the cyclic structure formed by AN and MMA units at a high temperature.¹⁵

Mechanical properties and rheological behavior

The tensile and impact strength of the terpolymers at different AN feed content are measured and the results are given in Table III. As can be seen from Table III, the tensile strength and impact strength of terpolymers increase with increasing AN feed content. The tensile strength and impact strength of PMMA in our study are 59.42 MPa and 2.35 kJ/cm^2 , respectively. It also can be seen that terpolymers with AN feed content over 15% exhibit a better impact strength than PMMA. As said above, the stiffness of the macromolecular chains was reduced by the small $-\text{CN}$ group of AN, and this contrib-

TABLE III
Mechanical Properties of Terpolymers

AN feed content (%)	Tensile strength (MPa)	Impact strength (kJ/cm^2)
0	30.8	1.83
5	34.2	2.15
10	39.3	2.40
15	43.0	2.35
20	47.0	2.40
25	52.0	3.40

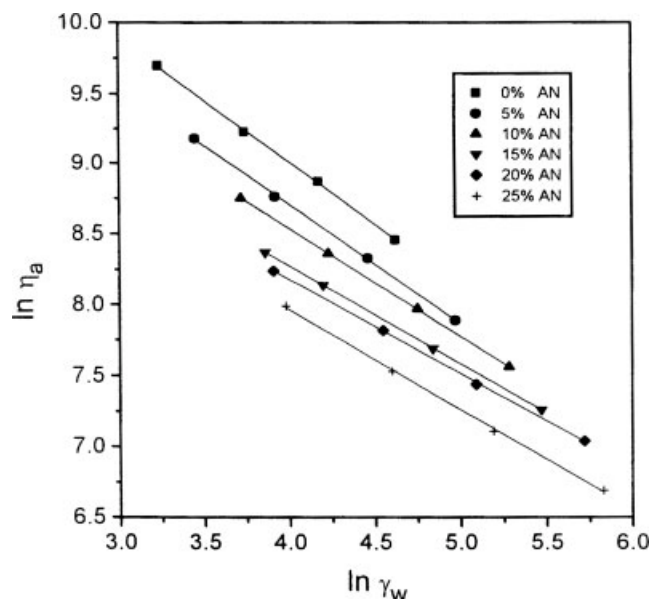


Figure 5 The apparent viscosity of polymers at different AN feed content.

uted to the increasing in tensile strength and increasing in impact strength with AN feed content.

The rheological behavior of the terpolymers was studied by using a Shimadzu Koka flow tester at 190°C. The plots of $\ln \eta_a$ versus $\ln \dot{\gamma}_w$ are given in Figure 5. As seen from Figure 5, the apparent viscosity η_a decrease with the increasing shear rate. It shows that the melt of the terpolymer resin is a pseudoplastic liquid. The apparent shear viscosity decrease with increasing AN feed content, meaning that the terpolymers have a better flowing ability. According to the Oswald–Dewal power law, $\tau_w = k_w^n$, and the rheological equation of state is $\eta_a = k_w^{n-1}$. The non-Newtonian parameter flow power n can be obtained. The n of terpolymers with 0, 5, 10, 15, 20, and 25% AN feed content is 0.113, 0.157, 0.238, 0.309, 0.334, and 0.397, respectively. This result suggests that the non-Newtonian property in the melt increase when AN added.

As shown in Table I, the molecular weight of terpolymers increase with the increasing of AN feed content, which would result in an increase in n_a . At the same time, however, a polymer in melt with less rigid backbone has a lower value of n_a . From the experimental results, it can be concluded that the bulk effect of AN is predominant over its molecular weight effect and polarity effect.

CONCLUSIONS

In this article, AN was introduced to the reaction system of MMA and ChMI. The AN was found to improve the conversion of the ChMI. Suspension polymerization produces terpolymers of homogenous chain structure as evidenced by the TBA method. While the tensile strength and impact strength increase with increasing AN feed content, T_g and T_{Vicat} decrease. But all the terpolymers exhibit a higher T_g than that of pure PMMA, and T_{Vicat} of terpolymers when AN feed content is in the range of 0–15% are higher than that of pure PMMA. The TGA results show that the thermal stability of MMA–ChMI copolymer is much better than pure PMMA, and the degradation temperature of terpolymers were enhanced by adding AN. The terpolymer in melt has a behavior of pseudoplastic liquid, and the apparent viscosity η_a of the melt decrease with increasing AN feed content, meaning that the terpolymers have a better flowing ability. The flow power n increased with AN feed content, suggesting that the incorporated AN increases the non-Newtonian property of the terpolymer in melts.

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