

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

Liting Yang,¹ Donghai Sun²

¹College of Chemical and Environmental Science, South China Normal University, Guangzhou, 510631, People's Republic of China

²Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 29 May 2005; accepted 15 July 2005

DOI 10.1002/app.22635

Published online 11 January 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *N*-cyclohexylmaleimide (ChMI) and styrene (St) were polymerized with methyl methacrylate (MMA) at different St feed content by suspension polymerization method. The glass transition temperatures (T_g) of the terpolymers were detected by torsional braid analysis (TBA). Two transition peaks in TBA curves of the terpolymers with a high St content illustrated that these terpolymers have a heterogeneous chain structure and the phase separation occurred. The lower transition temperature, T_{g1} , was assigned to the random St-MMA components, and the higher transition temperature, T_{g2} , was assigned to the St-ChMI units-rich segments. Thermogravimetric analyses (TGA) revealed that all the terpolymers showed a two-step degradation

process. The tensile strength of the terpolymers decrease with increasing St content while the impact strength tended to increase slightly. The rheological behavior of the terpolymers was also detected. The result illustrated that the terpolymers showed rheological behavior similar to that of pseudoplastic liquid. The apparent shear viscosity decreased with the increasing of St content. All terpolymers have a higher value of flow n than the poly(MMA-co-ChMI). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 918–922, 2006

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

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is the most popular commercial polymer used for glazing and optical application in the acrylic industry, 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, which 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.^{1–5} The incorporation of rigid polar maleimide structure in the macromolecular chain increase both the T_g and the degradation temperature of the modified PMMA. However, the coloration of these copolymers at high temperature has been pointed as an undesirable characteristic because the monomeric ChMI and the unreacted ChMI monomer in the resin. Several attempts had been made to solve the problem. Yuichi and coworkers⁶ 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. Shao-sheng and his coworkers⁷ introduced the styrene (less than 10 wt % of the monomers) to the polymerization system of ChMI and MMA to decrease the residual ChMI concentration in the copolymers. Their results suggested that the addition of St in the feed monomers made the copolymerization less difficult and ensured a high conversion of ChMI and a colorless resin. Though this method proved to be a useful technique to improve the light transmittance of poly(ChMI-MMA), other 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 St were synthesized by suspension polymerization method, and the thermal, mechanical, and rheological properties were evaluated.

EXPERIMENTAL

Material

N-cyclohexylmaleimide (ChMI) was provided as commercial product by Zhuozhou Haihui Chemicals Co. Ltd. Hebei Province, P. R. China and was recrystal-

Correspondence to: L. Yang (yanglt63@yahoo.com.cn).

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

Sample no.	Feed monomers (wt %)			Terpolymer component ^b (wt %)			$M_n/10^5$	$M_w/10^5$
	MMA	ChMI	St	MMA	ChMI	St		
1	80	20	0	85.26	14.74	0	1.32	7.03
2	75	20	5	77.79	16.15	6.06	1.25	7.03
3	70	20	10	71.89	17.51	10.6	1.44	7.97
4	65	20	15	66.81	18.14	15.05	2.2	7.91
5	60	20	20	60.79	19.37	19.84	1.54	7.81
6	55	20	25	55.03	19.52	25.45	0.96	6.52
7	50	20	30	49.34	19.66	31.00	1.20	5.88

^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.

lized from a mixture of alcohol and water and stored in absence of light before use. MMA, St, Polyvinyl alcohol (PVA1788), and BPO were supplied by Beijing Chemical Reagent Co. (Beijing, P. R. China). MMA and St were washed with aqueous sodium hydroxide to remove the inhibitor and then with water to attain neutrality. Polyvinyl alcohol (PVA1788) was used as suspending agent and used 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 St was carried out in a 3-necked flask equipped with a reflux condenser, a stirrer, and a thermometer. The solution of ChMI and BPO in MMA and St was charged into 300 mL solution of PVA in the 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 and the elemental analysis of nitrogen, hydrogen, and carbon was performed on a PE-240 elemental analysis test apparatus.

The \bar{M}_n and \bar{M}_w of the terpolymers were determined 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 narrowly 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 at a heating rate of 10°C/min in an air atmosphere for determining the onset of degradation (T_{ini}) and the maximum degradation rate temperature (T_{max}).

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 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, pushed 1 mm into the sample was taken as T_{vicat} .

The rheological behavior of the terpolymers was investigated by a Shimadzu Koka flow test apparatus. The temperature was fixed at 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 $100 \times 10 \times 5$ mm³ in size. The tensile strength (stress at yield) was measured at 25°C by using an electronic tensile tester 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 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 absorption at 500, 600, and 1500 cm⁻¹ assigned to the benzyl in St show the existence of St in the polymer. As seen from Figure 1, the peak at 1710 cm⁻¹ increases with increasing of St feed content, which suggests that the ChMI conversion increases with the increasing of St feed content. This result was proved by the elemental analysis results as shown in Table I. The terpolymers are composed of carbon, oxygen, hydrogen, and nitrogen. Nitrogen only comes from ChMI and oxygen only comes from MMA. So, the composition of terpolymer can be calculated from the elemental analysis results. The elemental analysis from which the compositions of the terpolymers were calculated were listed in Table II. 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

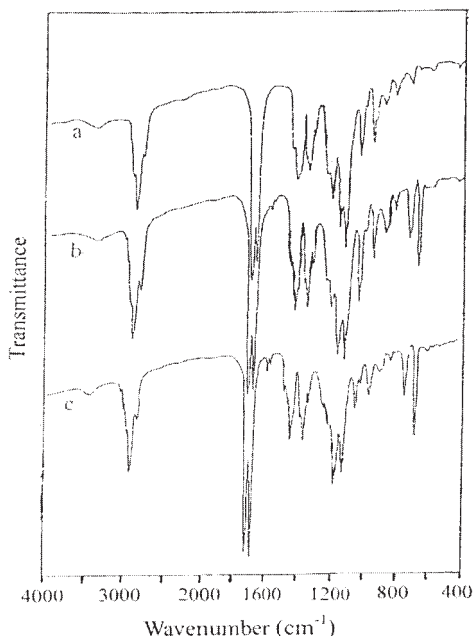


Figure 1 FTIR spectra of polymers. (a) MMA : ChMI = 80 : 20, (b) MMA : ChMI : St = 70 : 20 : 10, and (c) MMA : ChMI : St = 50 : 20 : 30.

in the terpolymer of ChMI/MMA/St. When St is introduced to the reaction system, the ChMI content is found to increase with increasing St feed content, suggesting that St makes ChMI to react easily. In comparison to the fact that the ChMI and MMA tend to form random copolymer, ChMI and St tend to form nearly alternating copolymer or homopolymer of individual monomers.⁶ The strong tendency for forming alternating copolymer⁶ is also depicted by the copolymerization reactivity ratios of $r_1 = 0.11$, $r_2 = 0.02$ for St (M_1) polymerization with ChMI (M_2). When St is added to the reaction system of ChMI and MMA, ChMI reacted with St prior to MMA, so that the resulting polymer will give different chain segments. The final product will give two T_g s and this result is proved by TBA analysis as shown in Figure 3.

The molecular weights at different St feed content were summarized in Table I. As seen from Table I, The highest molecular weight (\bar{M}_n , \bar{M}_w) was at 15% of St

TABLE II
Elemental Analysis Results

Sample no.	N (%)	C (%)	H (%)
1	1.153	61.327	7.958
2	1.263	63.106	7.901
3	1.370	64.736	7.805
4	1.419	66.238	7.764
5	1.515	67.892	7.716
6	1.527	69.642	7.766
7	1.538	71.402	7.786

TABLE III
 T_g and T_{vicat} of the Samples

Sample no.	T_{g1} (°C)	T_{g2} (°C)	T_{vicat} (°C)
I	N.D.	131.1	137.3
2	N.D.	132.0	137.0
3	N.D.	133.2	137.8
4	125.1	135.9	138.6
5	122.5	137.8	139.7
6	117.1	141.2	140.8

N.D.: Not detected.

feed content in weight and the molecular weight distribution (\bar{M}_w/\bar{M}_n) is 3.5. The molecular weight distribution (\bar{M}_w/\bar{M}_n) of terpolymers at 0, 5, 10, 15, 20, 25, and 30% St feed content are 5.3, 5.6, 5.5, 3.6, 5.1, 6.8, and 4.9 respectively.

Thermal properties

TBA technique was employed to detect the T_g s of the samples. T_g of PMMA synthesized under the same condition is 105.4°C, and that of sample 1 is 131.1°C, showing that ChMI increases the heat resistance of PMMA. The T_{vicat} of the terpolymers, as listed in Table III, is found to increase somewhat with the St content, illustrating the incorporated St can improve further the heat resistance of PMMA. In this study, the feed concentration of ChMI is fixed and the St concentration varied from 5 to 30 wt %. It was found that the glass transition peak in TBA curves became wider with the percentage of St unit until two peaks appeared at St concentration above 20 wt %. The TBA curves of terpolymers with 0, 10, 20, and 30% St feed content were shown in Figure 2. As can be seen from Figure 2, the lower glass transition temperature, T_{g1} , shifts toward a lower temperature and the higher one, T_{g2} , toward a higher temperature. The two T_g s, together with the T_{vicat} , are listed in Table III. The double peaks in TBA curves' mean phase separation occurred caused by immiscible components, suggest the terpolymers have a heterogeneous molecular structure.

In comparison to the fact that the ChMI and MMA tend to form random copolymer, ChMI and St tend to form nearly alternating copolymer or homopolymer of individual monomers.⁸ The strong tendency for alternation⁸ is also depicted by the copolymerization reactivity ratios of $r_1 = 0.11$, $r_2 = 0.02$ for St (M_1) polymerization with ChMI (M_2). When St is added to the reaction system of ChMI and MMA, ChMI reacted with St prior to MMA, so that St-ChMI unit-rich segments were formed at early stage during polymerization process. Poly(ChMI-St) was synthesized using the procedure described by Takayuki,⁸ at 80°C with a conversion of 59%. The monomer ratio of St:ChMI is 0.98:0.88. The resulting copolymer is expected to have

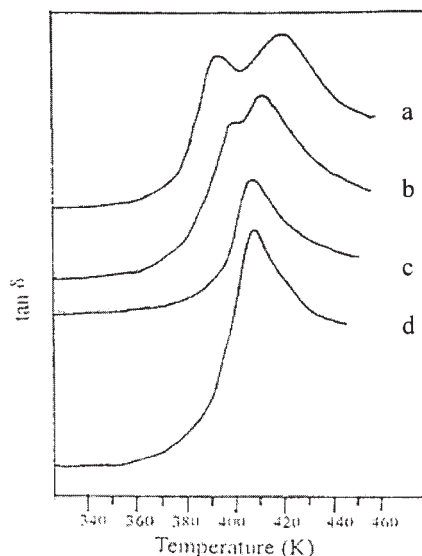


Figure 2 TBA curves of terpolymer Samples (a) MMA : ChMI = 80 : 20, (b) MMA : ChMI : St = 70 : 20 : 10, (c) MMA : ChMI : St = 60 : 20 : 20 and (d) MMA : ChMI : St = 50 : 20 : 30.

a nearly alternating molecular structure. Its T_g measured by TBA is 139.3°C, which is in agreement with the value of T_{g2} , so that T_{g2} is safely assigned to the glass transition temperature of ChMI-St-rich segments. On a sufficiently high concentration of St unit, i.e., above 20%, after the ChMI was almost consumed, St-MMA components formed. The T_g of poly(MMA-co-St) with various compositions has been studied by Ahuja⁹ and Beevers.¹⁰ Our experiment condition is close to that of Ahuja's, and T_{g1} of terpolymer with 20% St feed content is in agreement with any composition. Because of the unavoidable existence of ChMI units in these MMA-St-rich components, the T_{g1} is suggested to represent the T_g of MMA-St-rich components.

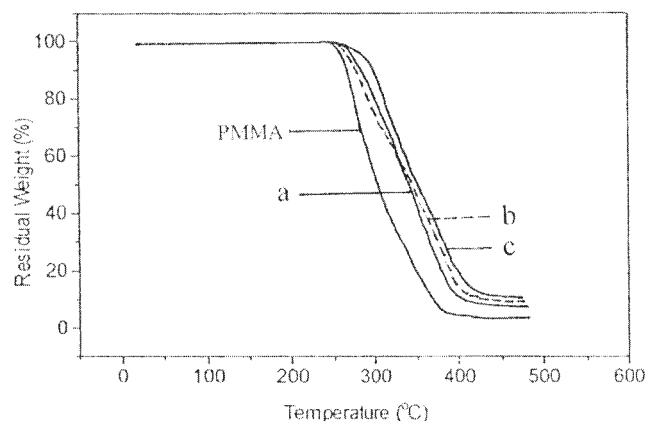


Figure 3 TGA curves of polymers (a) MMA : ChMI = 80 : 20 (b) MMA : ChMI : St = 70 : 20 : 10 (c) MMA : ChMI : St = 50 : 20 : 30.

TABLE IV
Thermal Degradation Temperature of the Terpolymers

St cont (wt %)	0	5	10	15	20	25	30
T_{max} (°C)							
T_{max1}	–	291.4	287.1	289.9	287.1	313.2	316.7
T_{max2}	–	376.2	379.0	367.2	384.9	373.6	379.0
T_{ini} (°C)	255.3	250.8	243.4	250.3	256.1	260.1	264.1

The Vicat soft temperature of terpolymers as shown in Table III is in the range of 137–141°C. The T_g and T_{vicat} of pure PMMA synthesized at same condition are 105.4 and 118°C respectively. The T_g s and T_{vicat} of the terpolymers as shown in Table III are much higher than that of PMMA.

Figure 3 shows the TGA curves of copolymer and terpolymers. The result for PMMA is also included as a comparison. 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. All terpolymers degrade via a two-step process. The initial degradation temperature (T_{ini}) and the two maximum degradation rate temperatures (the lower one, T_{max1} and the higher one, T_{max2}) are summarized in Table IV. T_{ini} is found to decrease with St concentration in a concentration region below 10%, whereas it increases with St content above 10%, i.e., the T_{ini} reaches a minimum when the feed monomer mixture contains around equimolar St and ChMI. T_{max} of poly(MMA-co-ChMI) with 20% ChMI feed content is 339.4°C. T_{max1} s of terpolymers are lower than the T_{max} of poly(MMA-co-ChMI) in all cases and is greatly increased when St feed content is above 20%. T_{max2} s seem to remain unaffected by the St concentration and are higher than the T_{max} of poly(MMA-co-ChMI). As seen in Figure 3, the ChMI-containing polymers have a better thermal stability than do PMMA.

Mechanical properties and rheological behavior

Tensile and impact strength of the terpolymers at different St contents are measured and the results are given in Table V. As can be seen from Table V, the tensile strength decreases with St feed content because of reduction in inter- and intra- molecular action. The

TABLE V
Mechanical Properties of the Terpolymers

St cont (wt %)	0	5	10	15	20	25	30
Tensile strength (MPa)	47.11	45.77	39.70	34.70	32.66	25.01	23.00
Impact strength (kJ/cm ²)	1.91	1.93	1.94	2.06	2.15	2.08	1.93

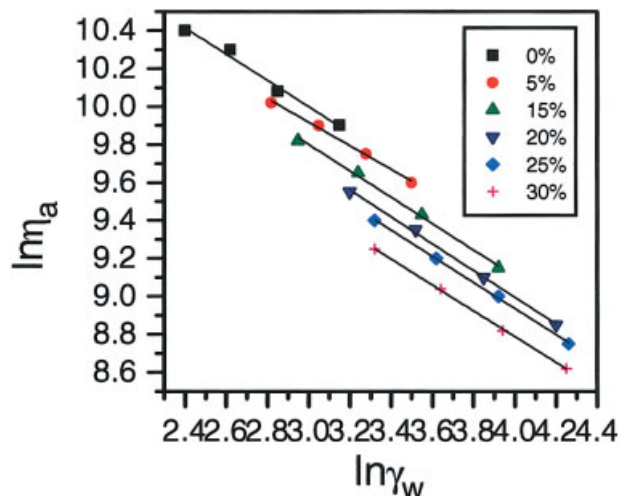


Figure 4 The apparent viscosity of polymers at different St feed contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

impact strength of the terpolymer tends to increase slightly with the increasing of St 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 4. As seen from Figure 4, 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 St content, meaning the terpolymers have a better flowing ability. According to the Oswald–Deval power law, $\tau_w = k\dot{\gamma}_w^n$, and the rheological equation of state¹¹ is $\eta_a = k\dot{\gamma}_w^{n-1}$. The non-Newtonian parameter flow power n can be obtained. The n of polymer with 0% St content is 0.28 and that of terpolymer is in the range of 0.30–0.32. This result suggests the non-Newtonian property in the melt increase when St added.

CONCLUSIONS

In this paper, St was introduced to the reaction system of MMA and ChMI. The St was found to improve the conversion of the ChMI. Suspension polymerization produces terpolymers of heterogeneous chain structure as evidenced by the phase separation detected by the TBA method. Terpolymers with a high St concentration were reported to be composed roughly of ChMI–St unit-rich components and St–MMA unit-rich component, as illustrated by their individual T_g s. The T_{vicat} of the terpolymers increase slightly with the increasing of St feed content. All terpolymers thermally degrade via a two-step process, showing the great influence of the incorporated St unit on the degradation behavior of those terpolymers. The tensile strength of the terpolymers decreases with the percentage of St unit, while and the impact strength of the terpolymers increases with the increasing of St content. The apparent decrease in shear viscosity with increasing St content indicates that the terpolymers have a better flowing ability.

References

1. Matsumoto, A.; Kuboya, T.; Otsu, T. *Macromolecules* 1990, 24, 4508.
2. Yang, L.; Sun, D.; Li, Y. *J Appl Polym Sci* 2002, 84, 1070.
3. Renu, B.; Veena, C.; Varma, I. K. *J Appl Polym Sci* 1993, 49, 31.
4. Yang, L.; Sun, D.; Liu, G. *Int J Polym Mater* 2003, 52, 611.
5. Yang, L.; Sun, D.; Li, Y.; Liu, G. Gao, J. *J Appl Polym Sci* 2003, 88, 201.
6. Yuichi, K.; Kazuo, K.; Koichi, N. *J Appl Polym Sci* 1997, 63, 363.
7. Shaosheng, D.; Yuezheng, W. *J Appl Polym Sci* 1999, 72, 1335.
8. Takayuki, O.; Akikazu, M.; Toru, K. *Polym Int* 1991, 25, 179.
9. Ahuja, S. K. *Rheol Acta* 1979, 18, 374.
10. Beevers, R. B. *Trans Faraday Soc* 1962, 58, 1465.
11. Arai, T. *A Guide to the Testing of Rheological Properties with Koka Flow Tester*; Maruzen: Tokyo, 1958; p 16.