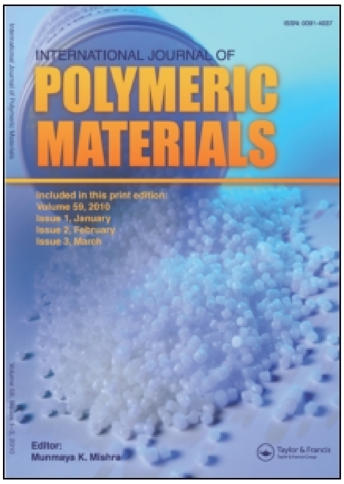

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Synthesis and thermoanalysis of suspension copolymer of N-cyclohexylmaleimide and methyl methacrylate

Liting Yang[a]; Donghai Sun[a]; Yanfang Li[a]; Jungang Gao[a]; Guodong Liu[b]
[a] Chemistry Department, Hebei University, PR China [b] Institute of Polymer Science and Engineering, School of Chemical Engineering, Hebei University of Technology, Tianjin, PR China

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SYNTHESIS AND THERMOANALYSIS OF SUSPENSION COPOLYMER OF N-CYCLOHEXYLMALEIMIDE AND METHYL METHACRYLATE

Liting Yang
Donghai Sun
Yanfang Li
Jungang Gao
Chemistry Department of Hebei University, PR China

Guodong Liu
Institute of Polymer Science and Engineering, School of Chemical Engineering, Hebei University of Technology, Tianjin PR China

Copolymers of N-cyclohexylmaleimide (CHMI) and Methyl Methacrylate (MMA), in which CHMI content ranged from 5–80% (in Wt.), were synthesized by suspension polymerization. The thermal properties of copolymer at different CHMI feed content were investigated by TBA and TGA. The results show that the glass transition temperature (T_g) and the decomposition temperature of copolymers increased with increasing CHMI feed content. $\bar{M}_n$ and $\bar{M}_w$ of copolymers were determined by GPC. The resultS show that there exists a maximum value when the CHMI feed content lay between 50 and 60%. The mechanical properties (tensile strength and impact strength) of the copolymers decreased with increasing CHMI content. The rheological behavior of copolymers in the melt was that of pseudo-plastic liquid, and the flow index n increased with increasing CHMI feed content from 5 to 30%.

Keywords: N-cyclohexylmaleimide, MMA; suspension polymerization, thermal analysis

INTRODUCTION

Since it has been found that N-substituted maleimide could polymerize with many vinyl monomers [1, 2], they have became

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Address correspondence to Liting Yang, Chemistry Department of Hebei University, Boading 071002, PR China. E-mail: gaojg@mail.hbu.edu.cn

interesting monomers to copolymerize with other monomers in order to obtain heat resistant resins. The incorporated five-member planar ring in the backbones of copolymer ensures higher T_g and higher thermal degradation temperature. So N-substituted maleimides, are widely used to enhance the heat resistance of polymers such as PSt [3–7], PVC [8–11], and PMMA [12–14].

Over the last 50 years, the use of PMMA has increased greatly because of its properties of excellent transparency, good thermoforming ability, good resistance to aging, corrosion and interesting biocompatibility characteristics. However, the low heat resistance of PMMA limited its application. Several monomers [15, 16] were developed to copolymerize with MMA to enhance the heat resistance of resulting resin, CHMI is the best one [17]. Most previous work focused on the kinetics of the copolymerization of CHMI and MMA and the determination of the reactivity ratios. However, there are few reports [18] on the relationship between the CHMI feed content and the properties of the copolymer such as thermal stability, mechanical properties and rheological behavior. In this work, copolymer of MMA and CHMI (in which CHMI feed content ranged from 5–80%) was synthesized by suspension polymerization and the effects of monomer composition on, $\bar{M}_n$, $\bar{M}_w$, T_g, thermal stability, mechanical properties and rheological behavior were investigated.

EXPERIMENTAL

Materials

CHMI (Zhuozhou Haihui Chemicals Co. Ltd., Hebei Province, P. R. China), a commercial product, recrystallized from mixture of alcohol and water, was dried before use. MMA was washed with aqueous sodium hydroxide to remove the inhibitor and then with water to neutral before use. Polyvinyl alcohol (PVA1788) was used as suspending agent and benzoyl peroxide (BPO) as initiator. Water used in all experiments were distilled and deionized water (DDW).

Suspension Polymerization

The copolymerization of MMA and CHMI was carried out in a three-necked flask equipped with a reflux condenser, a stirrer and a thermometer. Solution of CHMI in MMA was charged into solution of PVA in flask according to Table 1.

TABLE 1 Recipe of Suspension Copolymerization

Sample No.	0	1	2	3	4	5	6	7	8	9
MMA(g)	100	95	90	80	70	60	50	40	30	20
CHMI(g)	0	5	10	20	30	40	50	60	70	80
BPO(g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
PVA(0.08%)(ml)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DDW(ml)	300	300	300	300	300	300	300	300	300	300

The reaction was conducted at 80°C under stirring. After 4 h, the reaction was then kept at 100°C for an additional 1 h. The product was purified by washing with DDW then dried in vacuum oven at 80°C for 6 h. The overall percentage conversion was over 95%.

Analysis Methods

FTIR and Elemental Analysis

The FTIR analysis and elemental analysis were performed on a FTS-40 IR spectrophotometer and a PE-240 elemental analysis tester, respectively.

Gel Permeation Chromatography (GPC)

Molecular weights of copolymers were determined using a P200 GPC. Tetrahydrofuran was used as the following phase and the flow rate was 1.00 ml/min. The column was calibrated by using commercially available narrow distribution PSt. $\bar{M}_n$ and $\bar{M}_w$ were calculated by

$$\bar{M}_n = \frac{\sum H_i \cdot M_i}{\sum H_i} \quad \bar{M}_w = \frac{\sum H_i}{\sum (H_i/M_i)}$$

in which H is the peak height in the GPC spectrum.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out on a Shimadzu DT-40 Thermogravimeter, Half-loss weight temperature (T_{50}) was obtained when the weight loss of the copolymer reached 50% at a heating rate of 10°C/min in air atmosphere.

Torsional Braid Analysis (TBA)

T_g of copolymers were determined using a GDP-3 torsional braid analysis (TBA) unit at a heating rate of 2°C/min. T_g was taken from the maximum of logarithmic decrement in amplitude per cycle (Δ).

Rheological Behavior

The rheological behavior of copolymer was investigated using a Shimadzu koKa Flow Tester. The fixed temperature method was used. The nozzle diameter was 1 mm and the nozzle length was 10 mm. The weight of the test specimen was 1.5 g.

Mechanical Properties

The tensile test was performed using an electronic tensile tester. Tests were conducted at an extension rate of 10 mm/min at room temperature. The notch impact tests were carried out on an XCJ-40 impact tester.

RESULTS AND DISCUSSION

Composition of Copolymers

The IR spectra of copolymers of MMA and CHMI at different monomer feed proportions are shown in Figure 1. It was observed that the characteristic peak appeared around 1710 cm^{-1} which is the peak of stretching vibration absorption of carbonyl groups of CHMI in the chain of copolymer [14], gradually increased with increasing CHMI feed content, which indicated that the CHMI content in copolymer increased with increasing CHMI feed content.

The same tendency could also be seen from the elemental analysis results Table 2. CHMI in feed monomers was almost totally reacted with MMA when CHMI feed content was low. However, because of the lower activity of CHMI than that of MMA [19], the overall conversion of CHMI decrease, when the CHMI content in feed monomer was higher than 50%, and the resulting copolymers could not be used as transparent material because of their coloration at high temperature [12].

Molecular Weights

The $\bar{M}_n$ and $\bar{M}_w$ of the copolymers are shown in Table 3. In contrast to the homopolymer of PMMA, the molecular weight of the copolymer

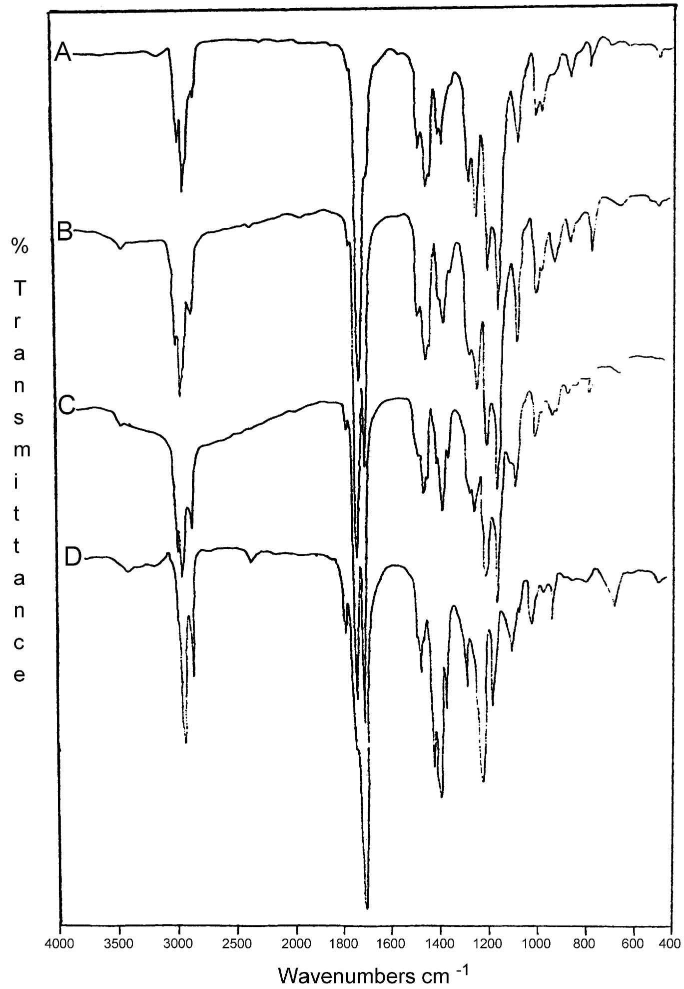

FIGURE 1 Spectrum of copolymers, CHMI feed content (% in Wt.) A: 0; B: 10; C: 50; D: 80.

decreased when a little CHMI charged into the feed monomers. This is because that CHMI is less active than MMA. It had been reported by Matsumoto and his coworkers [9] that $r_{CHMI} = 0.24$ and $r_{MMA} = 1.35$ in the copolymerization system with benzene as solvent and AIBN as initiator. As the CHMI content in feed monomers increased, the molecular weights of the copolymers increased slightly and there stayed a maximum value when CHMI feed content lay between 50–60%.

TABLE 2 Elemental Analysis Results

Sample No.	MMA:CHMI in monomers	MMA:CHMI incopolymer
0	100:0	100:0
1	95:5	94.9:5.1
2	90:10	89.8:10.2
3	80:20	79.3:20.7
4	70:30	71.0:29.0
5	60:40	59.8:40.2
6	50:50	54.3:45.7
7	40:60	39.5:60.5
8	30:70	33.5:66.5
9	20:80	25.1:74.9

TABLE 3 Average Molecular Weight of Copolymers at Different CHMI Feed Content

	CHMI feed content (% in Wt.)								
	0	10	20	30	40	50	60	70	80
$\bar{M}_w(10^5)$	1.06	0.51	0.77	1.12	1.65	1.78	1.69	1.50	1.57
$\bar{M}_n(10^4)$	2.8	1.06	1.61	3.41	5.46	6.50	6.51	4.81	4.53
$\bar{M}_w/\bar{M}_n$	3.79	4.81	4.78	3.28	3.37	2.74	2.60	3.12	3.46

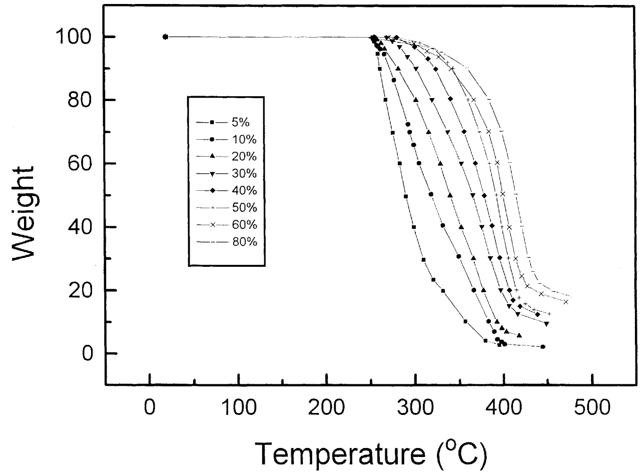

FIGURE 2 TGA curves of copolymers.

TGA

The thermal stability of the copolymers was characterized by thermal decomposition temperature. TGA curves are shown in Figure 2. The half weight loss temperature (T_{50}) plays an important role in characterizing the thermal stability of polymers. T_{50} of the copolymers of CHMI and MMA are shown in Table 4. Figure 3 indicated the relationship between T_{50} and CHMI feed content. The results in Table 4 and Figure 3 shows that T_{50} increased with the increase of CHMI feed content and all of the copolymers exhibited higher T_{50} than neat PMMA, which mean that all copolymers had a better thermal stability than PMMA. According to Table 4, T_{50} of PMMA was 296°C and that of the copolymer was 340.5°C when CHMI feed content was 20%, 44.5°C higher than that of neat PMMA. When the CHMI feed content was 80%, T_{50} of the resulting copolymer was 415.1°C, which mean that the copolymer shows a very good thermal stability. This is because the

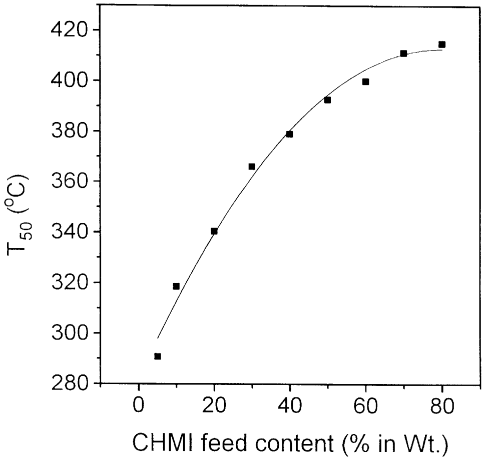

FIGURE 3 Relationship between T_{50} and CHMI feed content.

TABLE 4 T_{50} and T_g of Copolymers at Different CHMI Feed Content

CHMI feed content (% in Wt.)	0	5	10	20	30	40	50	60	70	80
T_{50}(°C)	295.6	290.8	313.8	340.5	366.1	379.1	392.8	400.1	415.1	424.0
T_{50}(°C)	115.0	116.1	118.7	124.2	129.0	137.0	153.1	166.6	187.5	209.1

incorporated five-member planar cyclic structure in the chain of copolymer enhances the thermal stability of the copolymer [20].

Glass Transition Temperature

The T_g of copolymer measured by TBA are shown in Table 4. The relationship between T_g and CHMI feed content is indicated in Figure 4. As seen from Table 4, all the copolymers had a higher T_g than neat PMMA. When CHMI feed content was 20%, the resulting copolymer exhibited a T_g of 124°C. The stiffness of the copolymer chain increased due to the planar ring and a big by-group. When CHMI units in copolymer chain increase, it is increasingly difficult for chain segments to rotate, which results in higher T_g. The T_g of the copolymers increased rapidly after CHMI feed content was over 40%, but from the

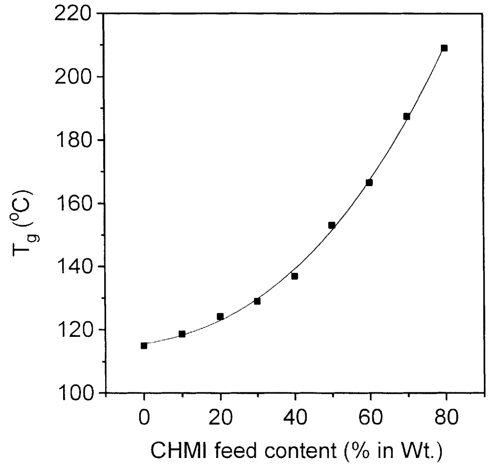

FIGURE 4 Relationship between T_g and CHMI feed content.

TABLE 5 Mechanical properties of copolymers at different CNMI feed content

CHMI feed content (% in Wt.)	0	5	10	20	30
Tensile strength (MPa)	59.42	59.01	57.59	46.36	19.94
Impact strent (kJ/cm^2	2.35	2.14	2.00	1.85	1.83
Flow Index n	0.163	0.170	0.179	0.337	0.364

economic point of view, the CHMI feed content should be controlled below 30%.

It should be noted that only one T_g of every suspension copolymer was detected by TBA, which is different from the copolymerization system of MMA and N-phenylmaleimide [21]. Though $r_{MMA} \cdot r_{CHMI} < 1$, which mean the copolymerization of CHMI and MMA had an alternating tendency, charge transfer complexes (CTC) were not detected in and the resulting copolymer was random instead of strictly alternating.

Mechanical Properties

Tensile and impact strength of copolymers at different CHMI feed content are shown in Table 5 and Figures. 5–6.

As seen from the results, the tensile and impact strength decreased with increasing CHMI feed content. The incorporated five-member ring and the big side-group (cyclohexyl) in CHMI unit decrease the interaction between molecular chains, which results in a low tensile strength. The low impact strength results from the high chain stiffness caused by CHMI unit.

Rheological Behavior

The experimental temperature was fixed at 190°C. Plots of ln η_a *versus* ln $\dot{\gamma}_w$ are given in Figure 7. As is seen from these figures, the apparent

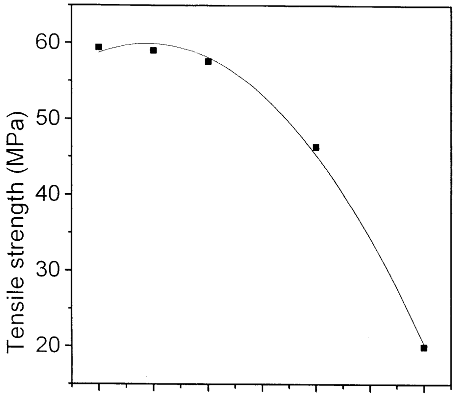

FIGURE 5 Relationship between tensile strength and CHMI feed content.

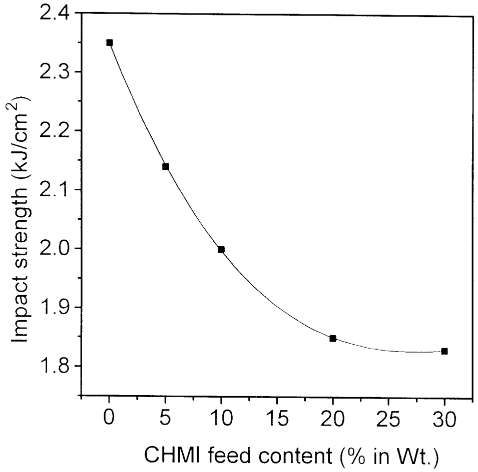

FIGURE 6 Relationship between impact strength and CHMI feed content.

viscosity η_a decreases with increasing shear rate $\dot{\gamma}_w$. It is shown that the flow behavior of copolymers in the melt is that of a pseudoplastic liquid and that the flow index n increases from 0.163 to 0.364 with increasing CHMI feed content from 0 to 30%. The incorporated CHMI units in the copolymer lower the interaction between the molecular chains and the flow ability of the copolymer melt improves.

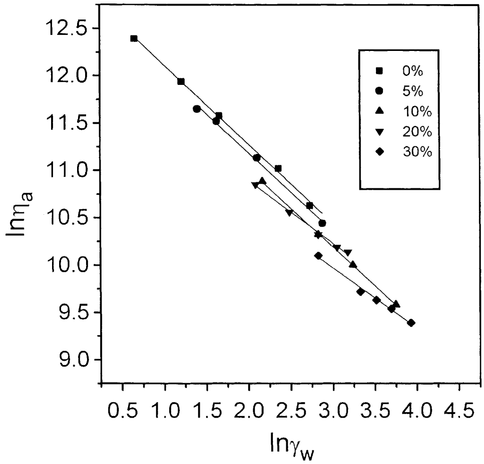

FIGURE 7 Rheological behavior of copolymers.

CONCLUSION

1. High CHMI content copolymer can be synthesized by suspension polymerization and the copolymer has a random structure evidenced by a single T_g.
2. CHMI is an effective monomer to improve the thermal properties of PMMA. T_g and T_{50} of the copolymer (MMA: CHMI = 80:20) was 124.2°C and 340.5°C, respectively, 9.2°C and 44.9°C higher than those of neat PMMA.
3. Copolymer of CHMI and MMA has a better processing ability than PMMA.
4. The mechanical properties (tensile strength and impact strength) are not greatly harmed if CHMI feed content is lower than 20%.

REFERENCES

[1] Iwatsuki, S. and Yamashita, Z. (1995). *Prog. Polym. Sci. Jpn.*, **2**, 1.
[2] Cowie, J., *Radical Initiated Alternating Copolymerization*, Plenum Press, New York 1985.
[3] Coleman, L. E. and Conrady, J. A. (1959). *J. Polym. Sci.*, **38**, 241.
[4] Yoshihara, M., Asakura, J. I. and Takahashi, H. (1980). *J. Macromol. Sci. Chem.*, **A20**, 123.
[5] Oishi, T., Iwahara, M. and Fujimoto, M. (1991). *Polym. J.*, **23**, 1409.
[6] Guorong, S., Zhixue, W. and Zuren, P. (1997). *J. Appl. Poly. Sci.*, **63**(12), 1535.
[7] Yuan, Y., Siegmann, A. and Narkis, M. (1995). *J. Appl. Poly. Sci.*, **61**, 1049.
[8] Otsuka, M. and Matsuoka, K. (1970). *Kogyo Kagaku Zasshi*, **73**, 1062.
[9] Horing, S., Jakawlew, S. and Ulblicht J. (1982). *Plaste and Kautschuk*, **29**, 622.
[10] Sergei, J. and Joachim, U. (1983). *Plaste Kautsch*, **30**, 305.
[11] Nakayama, M. (1994). Jp06 107734.
[12] Shaosheng, D. and Yuezhen, W. (1999). *J. Appl. Poly. Sci.*, **72**, 1335.
[13] Xulin, J. and Deyue, Y. (1999). *J. AppI. Poly. Sci.*, **74**, 1417.
[14] Shaosheng, D. and Yuezhen, W. (1999). *J. Appl. Poly. Sci.*, **74**, 516.
[15] Maeda, K. and Hirano, H. (1983). *Jpn. Kokai 83 87 104.*
[16] Nakai, Y., Shimomura, Y. and Tateyama, M. (1985). *Jpn. Kokai 85 76551.*
[17] Yuichi,K. and Kazuo, K. (1997). *J. Appl. Poly. Sci.*, **63**, 363.
[18] Usha, V. (1994). *Angrew. Macrmol. Chem.*, **221**, 1.
[19] Matsumoto, A., Kubota, T. and Otsu, T. (1990). *Macromlecules*, **23**, 4508.
[20] Richard, L. and Bernard, B. (2000). *J. Appl. Poly. Sci.*, **76**, 1888.
[21] Elsaabee, M. Z., Sabaa, M. W. and Naguib, H. F. (1989). *J. Macromol. Sci. Chem.*, **A24**(10), 1207.
[22] Xulin, J., Hongyun, T., Ping, X. and Deyue, Y. (1999). *J. Appl. Poly. Sci.*, **74**, 1293.