Synthesis and Characterization of Emulsion Copolymer of *N*-Cyclohexylmaleimide and Methyl Methacrylate

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ABSTRACT: Copolymers of *N*-cyclohexylmaleimide (ChMI) and methyl methacrylate (MMA) were synthesized by the emulsion semibatch copolymerization method. The effects of the monomer mixture composition on the average molecular weight ($\overline{M}_n$ and $\overline{M}_w$), glass transition temperature (T_g), degradation temperature, mechanical properties, and rheological behavior of the copolymers were investigated. The results show that $\overline{M}_n$ and $\overline{M}_w$ have maximum values when the ChMI feed content was about 20% (by wt). The degradation temperature and T_g of the copolymers increase with increasing ChMI moieties in the copolymer. The mechanical properties (tensile strength and impact strength) decrease with an increasing ChMI feed content. All copolymers in the melt show pseudoplastic behavior. The flow index n increases with an increasing ChMI feed content. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1070–1075, 2002; DOI 10.1002/app.10394

Key words: *N*-Cyclohexylmaleimide; MMA; emulsion polymerization; thermal analysis; mechanical properties; rheology

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is used for various applications for its excellent properties such as lack of color, high light transmittance, chemical resistance, and dimensional stability. However, PMMA has poor heat resistance and its glass transition temperature (T_g) is as low as 105°C. Studies have been carried out, since as early as the late 1930s, aimed at the preparation of heat-resistant PMMA resin. Copolymerization of MMA with other monomers has always been an important technique to modify the structure of its macromolecular chain and to improve the heat resistance of PMMA. Several monomers, such as α-methylstyrene[1] and maleic anhydride,[2] were developed for this purpose. In recent years, *N*-substituted maleimides have been selected as the most valuable monomers because these monomers contain a rigid planar ring and could enhance the T_g and the degradation temperature of copolymers effectively.[3,4] Among these monomers, *N*-cyclohexylmaleimide (ChMI) has been known as the best one in that it can enhance the heat resistance of PMMA without damage to its light transmittance.[5] Some works[6–9] focused on the polymerization behavior of MMA and ChMI have been carried out. However, the properties of these copolymers, such as the thermal stability and mechanical properties, have not been reported until now. Furthermore, it was observed in previous work[10,11] that the procedure of the emul-

Table I Recipe of Emulsion Copolymerization

Ingredient	Sample No.						
	1	2	3	4	5	6	7
MMA (g)	10.0	9.5	9.0	8.0	7.0	6.0	5.0
ChMI (g)	0	0.5	1.0	2.0	3.0	4.0	5.0
$K_2S_2O_8$ (g)	0.04	0.04	0.04	0.04	0.04	0.04	0.04
SLS (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DDW (mL)	30	30	30	30	30	30	30

sion polymerization method exerts a great influence on the structure and, thus, on the properties of the resulting copolymers, but the emulsion copolymerization of MMA and ChMI and the properties of the resulting copolymer have been unavailable so far. Copolymers of MMA and ChMI were synthesized in this work by semibatch emulsion polymerization (gradual addition of monomers method) and the effects of the monomer feed composition on the properties of copolymer such as the average molecular weight ($\overline{M}_n$ and $\overline{M}_w$), glass transition temperature (T_g), degradation temperature, mechanical properties, and rheological behavior were investigated.

EXPERIMENTAL

Materials

N-Cyclohexylmaleimide was supplied by ZhuoZhou Haihui Chemicals Co. Ltd. (Hebei Province, P.R. China) as a commercial product and was recrystallized twice from a mixture of alcohol and water. MMA was washed with aqueous sodium hydroxide to remove the inhibitor and then with water to neutral before use. Sodium lauryl sulfate (SLS), $K_2S_2O_8$, and $Al_2(SO_4)_3$ were AR grade (Beijing Chemical Regent Co., Beijing City, P.R. China). The water used in all experiments was distilled and deionized water (DDW).

Emulsion Copolymerization

Given amounts of SLS were dissolved in DDW in a 100-mL four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. The contents were effectively stirred and pure nitrogen was passed for 15 min. The temperature was increased to 80°C and the monomer mixture was added gradually to the flask together with the prepared solution of $K_2S_2O_8$ with vigorous stirring at 80°C for 1 h. After that, the reac-

tion vessel was maintained at that temperature for 0.5 h and then at 90–95°C for another 1 h. The reaction was stopped and precipitated by pouring into a 3% $Al_2(SO_4)_3$ solution. The product was obtained, by filtration, washing several times with hot water, and dried. Then, the copolymer was purified by washing with methyl alcohol for about 24 h to remove the residual ChMI monomer and SLS and then dried in a vacuum oven at 80°C before analysis. The conversion was measured gravimetrically and was always over 96%. The copolymerization procedures used the recipe given in Table I.
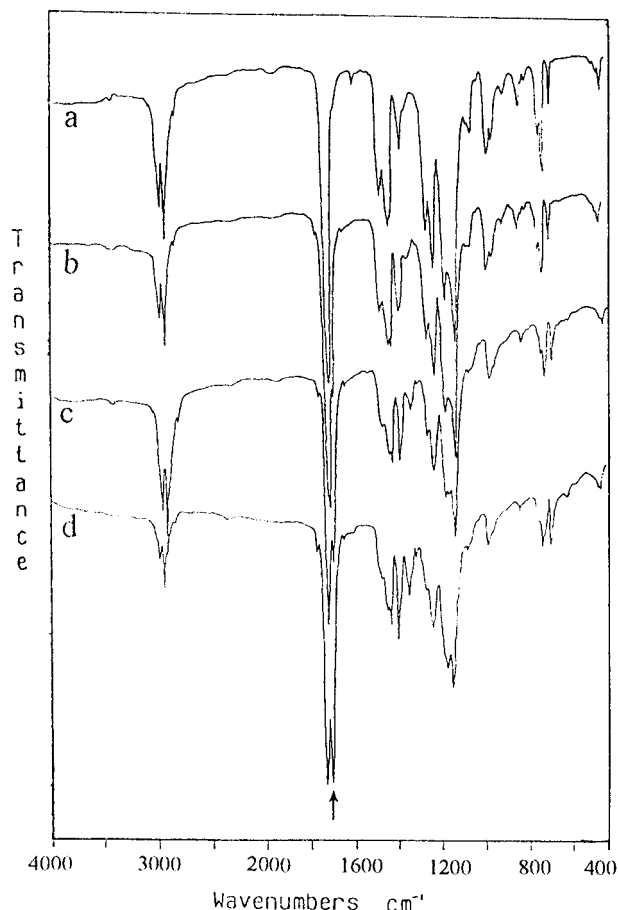
Copolymer Analysis

The FTIR analysis was conducted on an FTS-40 IR spectrophotometer and elemental analysis of nitrogen was performed on a PE-240 elemental analysis test apparatus. The ChMI content in the copolymer was calculated on the base of the nitrogen content. The $\overline{M}_n$ and $\overline{M}_w$ of the copolymer were determined using a P200 gel permeation chromatograph (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-distribution polystyrene. The $\overline{M}_n$ and $\overline{M}_w$ were calculated by

$$\overline{M}_n = \frac{\sum H_i M_i}{\sum H_i} \qquad \overline{M}_w = \frac{\sum H_i}{\sum \dfrac{H_i}{M_i}}$$

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

Thermogravimetric analysis (TGA) was carried out on a Shimadzu DT-40 thermogravimetric analyzer. The 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 an air atmosphere.

The glass transition temperature (T_g) of the copolymers was measured by torsional braid

Figure 1 FTIR spectra of polymers: (a) PMMA; (b) MMA : ChMI = 90 : 10; (c) MMA : ChMI = 80 : 20; (d) MMA : ChMI = 70 : 30.

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 the logarithmic decrement in amplitude per cycle (Δ).

The rheological behavior of the copolymers 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 tensile tests were performed using an electronic tensile tester at room temperature. The extension rate was 10 mm/min. The notch impact tests were carried out on an XCJ-40 impact tester under the same conditions.

RESULTS AND DISCUSSION

Copolymer Composition

IR spectra of poly(MMA-*co*-ChMI) at different monomer mixture proportions are shown in Figure 1. With the incorporation of ChMI units, the most significant feature is the appearance of the absorption peak at 1710 cm^{-1}, which is the peak of stretching vibration absorption of carbonyl groups of ChMI units in the backbone of the copolymer.[9] It is observed that the peak at 1710 cm^{-1} gradually increases with an increasing ChMI feed content. When no ChMI is fed, there is no absorption at 1710 cm^{-1} on the FTIR spectrum. This indicates that the ChMI content in the copolymer increased with an increasing ChMI feed content.

The elemental analysis results are listed in Table II. As seen from the data, the ChMI feed content is almost the same as is the ChMI content in the copolymer and it can be used to estimate the ChMI content in the copolymer.

Average Molecular Weight

Molecular weights of copolymers at different ChMI feed content are presented in Table III. Both the $\overline{M}_n$ and $\overline{M}_w$ increased with an increase of the ChMI content at a low ChMI content, and stayed at maximum values of $\overline{M}_n$ and $\overline{M}_w$ when the ChMI content was about 20%.

As is known, emulsion polymerization reactions take place mainly in micelles and only one active radical can be tolerated in it. So, the micelle will contain either one or no radical at any one time. The rate of the "on–off switching" is controlled by both the rate of radical production and the number of the micelles in the reaction medium. So, for a fixed initiator concentration and temperature, the chain length, and thus the molecular weight of the polymer, is a function of the rate of radical propagation ν_p and is not affected by other variations.[12] ν_p is a function of the monomer feed ratio if the reactivity ratios are fixed. As reported, it will be a maximum at the proper monomer composition. The molecular

Table II   Elemental Analysis Results

MMA : ChMI (by Weight)	
Calculated Results	Experimental Results
100 : 0	100.0 : 0.0
95 : 5	94.8 : 5.2
90 : 10	90.5 : 9.5
80 : 20	81.9 : 18.1
70 : 30	71.6 : 28.4
60 : 40	61.1 : 38.9

Table III   Molecular Weight of Copolymers

	ChMI Feed Content (Wt %)					
	0	10	20	30	40	50
$\overline{M}_w$ (10^5)	1.24	1.02	1.71	1.53	1.26	1.15
$\overline{M}_n$ (10^4)	4.15	4.03	6.25	5.38	2.57	1.66
$\overline{M}_w/\overline{M}_n$	2.99	2.53	2.74	2.84	4.9	6.93

weight of the copolymer is affected mainly by the monomer feed composition when the reaction temperature, emulsifying agent, and initiator concentrations are fixed and should have a maximum value at the proper monomer ratio. This is the reason why the molecular weight of these copolymers had a maximum value when the ChMI feed content was 20% or so.

TGA

The thermal stability of the copolymers was arbitrarily defined as a function of the initial thermal degradation temperature (T_i) and the T_{50} value. The TGA curves are shown in Figure 2. It is known that PMMA is liable to degrade at high temperature. The T_i and T_{50} of PMMA were 257.1 and 305.6°C, respectively, in our study. It can be observed, from the TGA curves, that the T_i and T_{50} clearly increase with an increasing ChMI feed content. Figure 3 illustrates the relationship between T_{50} and the ChMI feed content. As seen from Figure 3, the T_{50} of the copolymers increase

linearly with an increasing ChMI content. The linear relationship between T_{50} and the ChMI feed content is expressed as follows:

$$T_{50}(°C) = 302.92 + 1.977 \text{ ChMI (wt %)}$$

The T_{50} value is thus enhanced by about 1.977°C per 1 wt % of ChMI. When the ChMI feed content is 20%, the T_i and T_{50} of the resulting copolymer are 274.2 and 340.4°C, respectively, 17.1 and 34.8°C higher than those of neat PMMA, which means the copolymer exhibits a better thermal stability than that of PMMA. Obviously, it is the incorporated five-member cyclic structure in the copolymer chain that improves the materials' thermal stability.[13]

Glass Transition Temperature

The glass transition temperatures, T_g's, of the copolymers are considerably higher than the value of 105.4°C for PMMA itself, as can be seen
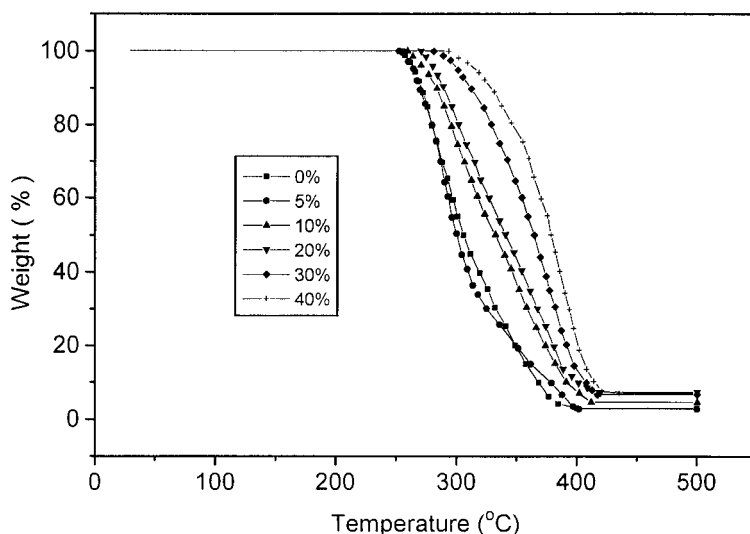
Figure 2   TGA curves of copolymers at different ChMI feed content.

from Figure 4. At a level of ChMI incorporation of as low as 5 wt %, the T_g was higher by 15.5°C. Then, the T_g's increase gradually with further addition of ChMI. This is because even a low level of the bulky ChMI units, incorporated into the polymer chain, can significantly block the rotation of the chain segments. The stiffness of the copolymer chains increased gradually thereafter with increasing ChMI units, resulting in a gradual increase of the T_g.
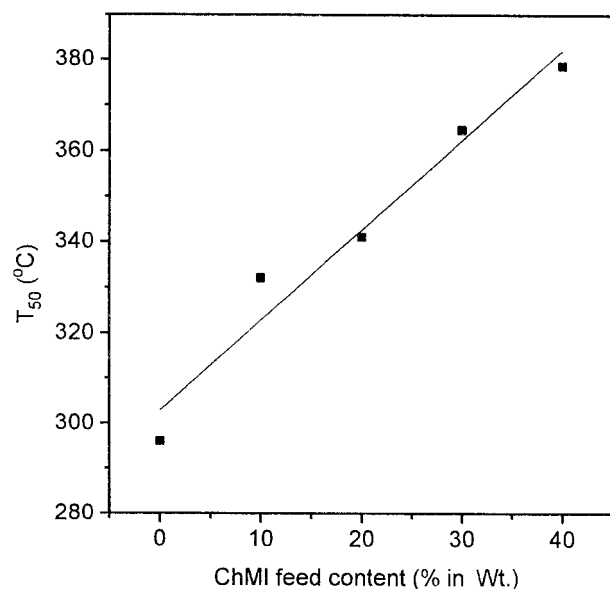
Mechanical Properties

Tensile and impact strengths of the copolymers at different ChMI content are given in Table IV. As can be seen from Table IV, the tensile and impact strength decrease as the ChMI feed content increases from 0 to 30%. When the ChMI feed content was 20%, the tensile strength and impact strength of resulting copolymer is, respectively, 42.0 MPa and 1.96 kJ/cm^2, 17.4 MPa and 0.39 kJ/cm^2 lower than that of PMMA.
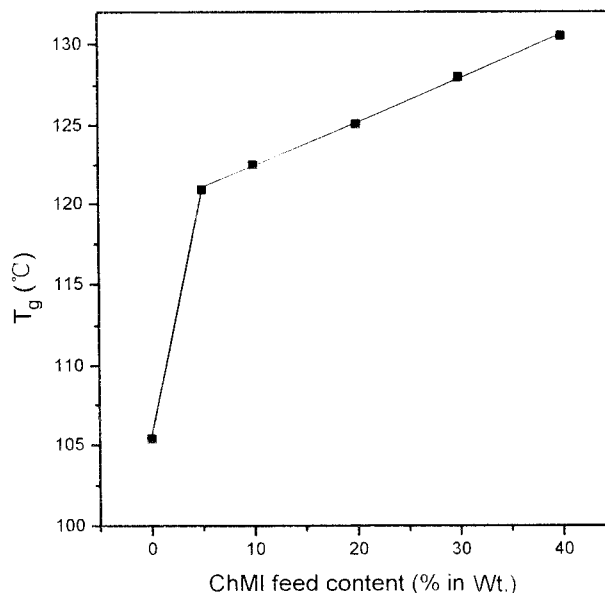
The decrease in the tensile strength may result from the bulky cyclohexyl side group, lowering the interaction between chains. The reason for the decrease of the impact strength is the high chain stiffness caused by the ChMI moieties.

Rheological Behavior

The rheological behavior of the copolymers was measured at 190°C. Plots of ln η_a versus ln γ_w are

Figure 4   Relationship between T_g and ChMI feed content.

given in Figure 5. As shown in the figure, the apparent viscosity η_a decreases with an increasing shear rate γ_w, which means that the copolymers in the melt show pseudoplastic behavior. The flow index n, as listed in Table IV, increases from 0.163 to 0.484 as the ChMI content increases from 0 to 30%. In addition to the original influence of the ChMI units, the increasingly broader molecular weight distribution, as shown in Table III, may also be responsible for the increase of n in the range of the shear rate in our work.

Generally speaking, the factors that cause the T_g to increase will result in a higher viscosity value. The principle, however, cannot be applied to the copolymer under study for, as illustrated in Fig. 5, the η_a decreases with increasing ChMI moieties. This can be attributed to the fact that the nonpolar six-member side group, cyclohexyl, lowers the interactions between the molecular chains. Meanwhile, less entanglement between the macromolecular chains, caused by the rigid maleimide structure,[14] can be thought to be responsible for the decreased η_a value. Furthermore, the increasingly broader molecular weight distribution of the copolymer can also contribute to the lowered η_a.

Figure 3   Relationship between T_{50} and ChMI feed content.

CONCLUSIONS

1. The IR and elemental analysis results show that semibatch emulsion copolymerization

Table IV   Mechanical Properties and Flow Index _n_ of Copolymer

| Property	ChMI Feed Content (Wt %)				
	0	5	10	20	30
Tensile strength (MPa)	59.4	49.6	47.7	42.0	23.8
Impact strength (kJ/cm^2)	2.35	2.18	2.15	1.96	1.07
Flow index _n_	0.163	0.184	0.345	0.465	0.484

of MMA and ChMI produces copolymers of a homogeneous chain structure.

2. ChMI is a valuable monomer to improve the thermal properties of PMMA. The glass transition temperature and degradation temperature of the copolymers are greatly enhanced by the incorporation of ChMI.

3. Copolymers of MMA and ChMI show pseudoplastic rheological behavior. The flow index n increases and the apparent viscosity η_a decreases with increasing ChMI content, which means that the incorporated ChMI can improve the processing ability of the resulting resin.

4. Mechanical properties (tensile strength and impact strength) of emulsion copolymers decrease with an increasing ChMI feed content. When the ChMI feed content was 20% (by weight), the tensile strength and impact strength of the resulting copolymer, 42.0 MPa and 1.96 kJ/cm^2, respectively, are only moderately reduced.

REFERENCES

1. Nakai, Y.; Shimomura, Y.; Tateyama, M. Jpn. Kokai 8 576 551, 1985.
2. Maeda, K.; Hirano, H. Jpn. Konkai 8 381 104, 1987.
3. Matsumoto, A.; Kubota, T.; Otsu, T. Macromolecules 1990, 24, 4508.
4. Usha, V.; Varma, I. K.; Bhayani, G. G.; Sinha, T. J. M Angew Macromol Chem 1994, 1, 221.
5. Yuichi, K.; Kazuo, K.; Koichi, N. J Appl Polym Sci 1997, 63, 363.
6. Xulin, J.; Hongyun, T.; Ping, X.; Deyue, Y. J Appl Polym Sci 1999, 74, 1293.
7. Xulin, J.; Hongyun, T.; Ping, X.; Deyue, Y. J Appl Polym Sci 1999, 74, 1417.
8. Shaosheng, D.; Yuezhen, W. J Appl Polym Sci 1999, 72, 1335.
9. Shaosheng, D.; Yuezhen, W. J Appl Polym Sci 1999, 74, 516.
10. Yuan, Y.; Siegmann, A.; Narkis, M.; Bell, J. P. J Appl Polym Sci 1996, 61, 1049.
11. Yuan, Y.; Siegmann, A.; Narkis, M.; Bell, J. P. Polym Adv Tech 1995, 6, 675.
12. Cowie, M. G. Polymers: Chemistry and Physics of Modern Materials; Chapman and Hall: New York, 1991.
13. Richard, L.; Bernard, B. J Appl Polym Sci 2000, 76, 1888.
14. Tordjeman, P.; Halary, J. L.; Monnerie, L. Polymer 1995, 36, 1627.
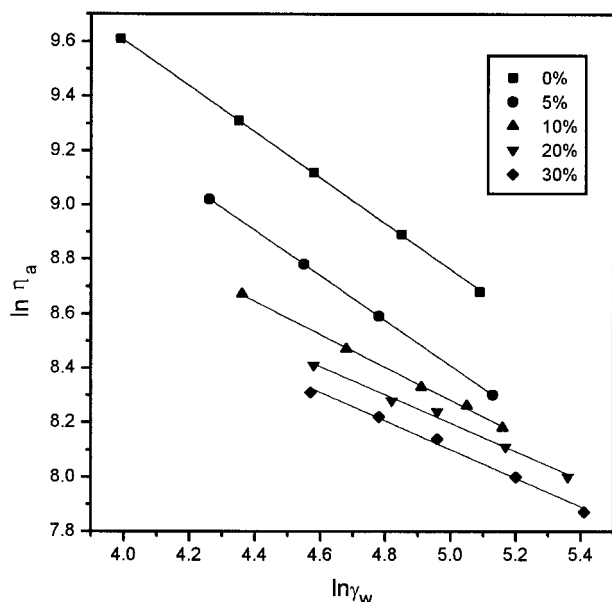
Figure 5 Viscosity of copolymers at different ChMI feed content.