

Graft Modification of Highly Chlorinated Polyethylene (HCPE) with Methyl Methacrylate by the Mechanochemistry Reaction. I. Synthesis and Characterization

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ABSTRACT: Highly chlorinated polyethylene-graft-methyl methacrylate (HCPE-g-MMA; HCPE with chlorine contents > 60%), obtained by a mechanochemistry reaction, is discussed in detail. A two-roll mill was used in the process. The reaction conditions affecting the structure of HCPE-g-MMA copolymers were measured in terms of calculation of graft efficiency (GE), graft degree (GD), and copolymerization rate/homopolymerization rate (R_c/R_h) by ¹H-NMR spectroscopy. Based on these results, it is concluded that the chlorine contents of

HCPE, the additional amount of MMA, and the mechanochemistry reaction time all have impacts on the structure of the polymer. The results also confirm that grafting is very much favored by the mechanochemistry reaction. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 811–816, 2003

Key words: polyethylene (PE); graft copolymers; copolymerization; NMR; highly chlorinated polyethylene (HCPE)

INTRODUCTION

Chemical modification of synthetic polymers offers a new possibility to improve the chemical and physical properties of original polymers. Grafting is one of the most useful methods for this purpose. When chlorinated polyethylene (CPE) is grafted with methyl methacrylate (MMA), the chemical and physical properties of the copolymer (CPE-g-MMA) will change compared with the original CPE. Over the past several years, much attention has been devoted to synthesizing and characterizing CPE (with a chlorine content of ~35%) graft copolymers, for instance CPE-g-MMA.^{1–5} However, little information concerning highly chlorinated polyethylene (HCPE) graft copolymers is available to us beyond our own work.

CPE graft copolymers have been synthesized by several methods, for examples, by graft reaction in solution^{1–3} and in water,⁵ and by the mechanochemistry reaction.⁴ In this investigation, the mechanochemistry method was carried out with a two-roll mill, where the two-roll mill was used as a chemical reactor for chemical modification of host polymers or the synthesis of new polymers. The mechanochemis-

try reaction is an effective way to introduce other functional groups into a polymer, and a wide variety of materials have been prepared in this way.^{6–9} We have found that it is economical and convenient to use a two-roll mill for the mechanochemistry reaction because new functional polymers can be produced without building a new facility, the reaction time is relatively short, and the costs of solvent recovery or wastewater cleanup can be avoided. In addition, polymers with a higher graft degree (GD) can be produced by this method.

In the mechanochemistry reaction, polymer molecules are broken with shearing stress into macroradicals, with the active center at the ends of the chain. Because macroradicals and heat are produced by shearing stress, the monomers begin polymerization by forming a blend system that includes HCPE block copolymer, HCPE graft copolymer, HCPE, polymethyl methacrylate (PMMA), and MMA. In this blend, block copolymers are the largest and graft copolymers are the smallest in quantity because only a few macroradicals hold free radicals on the side of the chain.^{6,7} Here we use the term HCPE-g-MMA for both MMA and HCPE copolymers, although, in fact, HCPE-g-MMA consists of HCPE-block-MMA and HCPE-graft-MMA.

To confirm and characterize HCPE-g-MMA, it is necessary to separate the MMA homopolymer from the blend system. There are many methods to purify a polymer system.^{10,11} The extraction method is gener-

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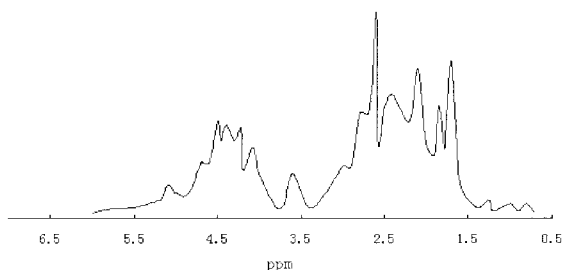


Figure 1 $^1\text{H-NMR}$ spectrum of insoluble substance in trichloromethane.

ally the Soxhlet extraction. The disadvantage of extraction is that a small amount of homopolymer remains in the system, resulting in overestimation of GD values. Similar results have been reported¹² with regard to the separation of CPE–styrene graft copolymer systems. In this study, the precipitation method was used to separate PMMA from the system. This method should ensure that only HCPE and HCPE-g-MMA are precipitated and PMMA is completely left in solution, but a little bit of HCPE-g-MMA copolymer might be kept in solution together with MMA homopolymer.¹³ Unlike the extraction method, the existence of copolymer in the system can be confirmed with the separating method because there is no interference of PMMA. However, the separating method can result in an underestimated GD of HCPE-g-MMA.

To characterize the procedure of synthesizing HCPE-g-MMA, measurements of GD and graft efficiency (GE) are necessary. Nuclear magnetic resonance (NMR) spectroscopy is a frequently used technique for characterizing the structure of polymers containing chlorine.^{14–16} In our investigation, the GD, GE, and ratio of copolymerization rate to homopolymerization rate (R_c/R_h) of all specimens were calculated from their $^1\text{H-NMR}$ spectra. It was believed that the H content in HCPE was constant in the graft process. Therefore, the amount of MMA in HCPE-g-MMA samples can be quantitatively determined by measuring the methoxy peak areas in their $^1\text{H-NMR}$ spectra.

A procedure for synthesizing HCPE-g-MMA is discussed. The focus areas include the influence of the amount of monomer, chlorine contents of HCPE, and mechanochemistry reaction time on GD, GE, and R_c/R_h . The relationship between modified polymer structures and properties will be reported in another paper.¹⁷

EXPERIMENTAL

Material

Methyl methacrylate (MMA) was obtained commercially from Second Chemical Reagent Works in Tian Jing, and methanol and trichloromethane were obtained from Chain and Jiang Shan Chemical Reagent

Company in Qing Dao, Chain. MMA was washed in an 8 wt % aqueous solution of NaOH three times to eliminate impurities, and then was washed again with distilled water to achieve pH 6–7. High-density polyethylene (HDPE; melt index, 0.5) was purchased from Chain Shi-hua Liao-yan Shi You Hua Xian Company.

HCPE and HCPE-g-MMA system preparation

Two general procedures for the preparation of HCPE and HCPE-g-MMA system are illustrated, respectively, by the following two examples: (1) 50 g of HDPE and 5 g of isolated agent (such as SiO_2 , MgO , or CaHPO_4) were put in a 500-mL three-necked round-bottomed flask equipped with a stirring bar. Nitrogen gas was introduced into the stirred mixture for 10 min before exiting. Then chlorine gas was continuously introduced into the system, and the temperature of the system was increased simultaneously. The process of the chlorination reaction is a gas–solid reaction, and the reactive pressure is normal pressure. Chlorination was performed to 20% chlorine content at 60–80°C, to 40% chlorine content at 80–120°C, and to > 60% at 120–140°C. After chlorination was finished, the temperature of the system dropped to < 100°C, and nitrogen gas was introduced into the system to replace residual chlorine gas. In the process of chlorinating, the side product, HCl, was carried out from the system by the chlorine gas and absorbed by NaOH water solution. (2) 20 g of MMA and 100 g of HCPE with 61.7% chlorine content were mixed thoroughly at room temperature before being masticated. The mixture was then added into a two-roll mill and masticated for 15 min. Next, the sample was drawn from the machine. The temperature of the two-roll mill was kept < 40°C by adding cool water, but the temperature between the two roll was > 40°C due to the shearing stress. The two-roll mill had dimensions of $\phi 160 \times 320$ mm, and rotary speeds of 24.4 rpm for the front roller and 32 rpm for the back roller.

Separating monomers and homopolymers

In the process of separating out monomers, the sample was first dissolved in trichloromethane, methanol was

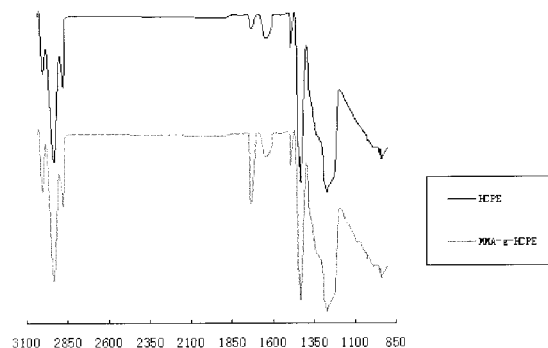


Figure 2 IR spectra of HCPE and MMA-g-HCPE.

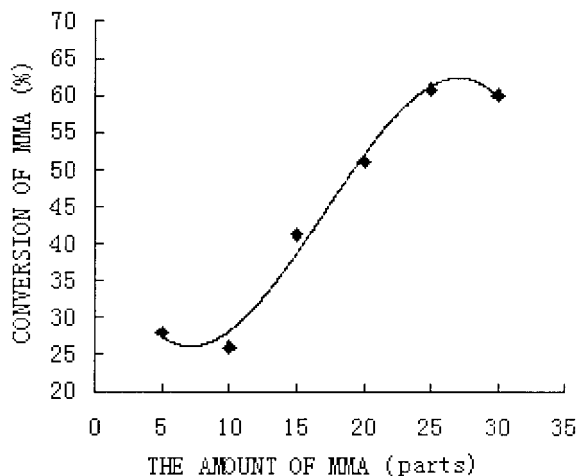


Figure 3 Conversion of MMA with the amount of MMA. The chlorine contents: 63.3% Wt%; reaction time: 15 minutes.

added to the trichloromethane solution to precipitate polymers, and the solution was separated. The addition of methanol separation of the solution was repeated until the chlorine content of the solution was < 0.5%. All of the precipitate was dried and dissolved again in trichloromethane. The procedure was repeated five times. The results show that no monomer remained in the system with reaction times of > 8 min in a two-roll mill.

Some samples of the HCPE-g-MMA system that were free from MMA were dissolved in trichloromethane; the sample/trichloromethane ratio (w/v) was ~1:4. Methanol was then added in a dropwise manner (methanol/trichloromethane = 1:4, v/v) to precipitate the polymer, except for PMMA. The precipitate was separated by centrifugation and dried. The dried precipitate was dissolved in trichloromethane again and the aforementioned procedure was repeated five times. The final product was dried in a vacuum oven at 60°C for 24 h.

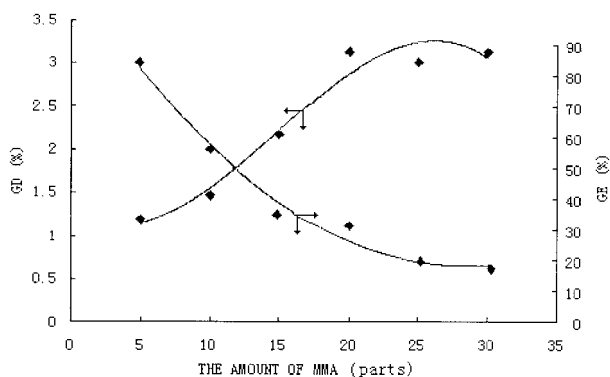


Figure 4 GD and GE of MMA with amount of MMA. The chlorine contents: 63.3% Wt%; reaction time: 15 minutes.

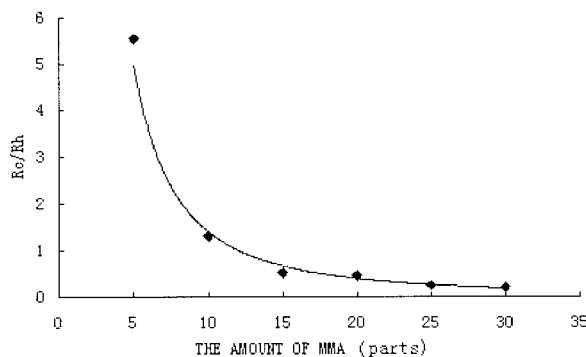


Figure 5 Rc/Rh of MMA with the amount of MMA. The chlorine contents: 63.3% Wt%; reaction time: 15 minutes.

Measurement and characterization

The ¹H-NMR spectra of HCPE-g-MMA, determined with a Varian UNITY-plus 400 NMR spectrophotometer, are shown in Figure 1. The spectra indicate a resonance at 3.63 ppm for the methoxycarbonyl proton.¹⁶ The MMA content in HCPE-g-MMA copolymers was calculated from the integral of this resonance and the total integral from ~0.95 to 5.70 ppm. In addition, the ratio of the amount of MMA grafted onto HCPE to the amount of HCPE (GD), the ratio of MMA grafted onto HCPE to the total polymerized MMA (GE), and the ratio of the rates of copolymerization to homopolymerization (R_c/R_h) were determined by calculation (eqs. 1–4).

$$MMA\% = 1/3 S_m \times 101.1 \times S_m / \{ (S - 2S_m) / H\% + 1/3 S_m \times 101.1 \} \quad (1)$$

where MMA% and H% are MMA and H percentage by weight, respectively, S and S_m are the accumulative total of integral areas from 0.95 to 5.70 ppm and the integral area at 3.63 ppm, respectively, and the molecular weight of MMA is 101.1.

$$GE = MMA\% \times \{ HCPE(g) + MMA(g) - loss\ weight \} / (MMA(g) - loss\ weight) \quad (2)$$

$$GD = MMA\% \times \{ HCPE(g) + MMA(g) - loss\ weight \} / HCPE(g) \quad (3)$$

$$R_c/R_h = GE / (1 - GE) \quad (4)$$

In eqs. 2 and 3, weight loss is taken into consideration because of the volatilization loss of MMA in the mechanochemistry reaction.

Conversion was calculated as follows:

$$Conversion\ \% = \frac{\text{added amount of MMA} - \text{loss weight of MMA}}{\text{added amount of MMA}}$$

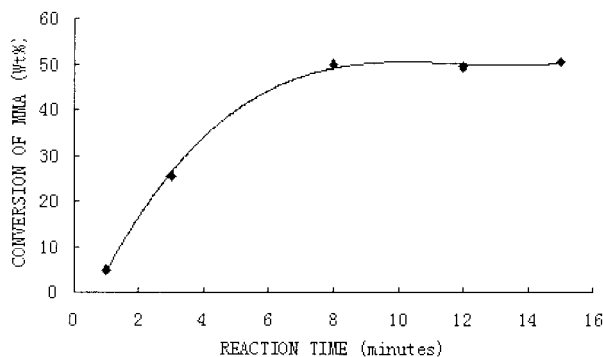


Figure 6 Conversion of MMA with different reaction times. The chlorine contents: 61.7% Wt%; the amount of MMA: 20 parts.

$$- \text{remaining monomer of MMA}) / \text{added amount of MMA} \times \% \quad (5)$$

RESULTS AND DISCUSSION

Existence of HCPE-g-MMA copolymers

In our study, HCPE and MMA were well mixed and masticated with a two-roll mill for 10 min, and then PMMA was separated. The IR spectra of the HCPE-g-MMA system that was free from PMMA and HCPE are shown in Figure 2. Comparing the IR spectrum of HCPE with that of the HCPE-g-MMA system without PMMA indicates an obvious absorption at 1730 cm^{-1} in both samples, which might be due to the contribution of the $\text{C}=\text{O}$ group in MMA. The absorption at 1730 cm^{-1} in the HCPE spectrum is unexpected, and may be explained by an oxidizing reaction taking place while masticating HCPE.

The absorption at 1730 cm^{-1} in the spectrum of the HCPE-g-MMA system without PMMA is much larger than that at 1603 cm^{-1} . On the other hand, the opposite result is evident for HCPE. These results support the hypothesis that HCPE-g-MMA copolymers are

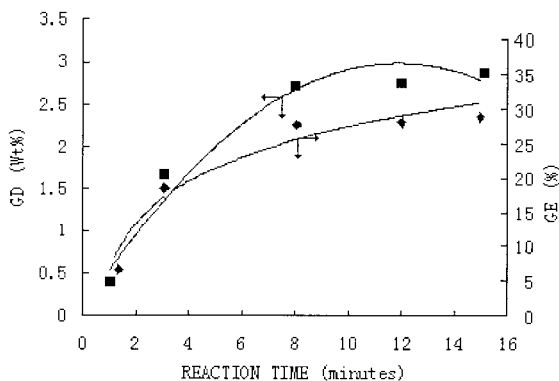


Figure 7 GD and GE of MMA with different reaction times. The chlorine contents: 61.7% Wt%; the amount of MMA: 20 parts.

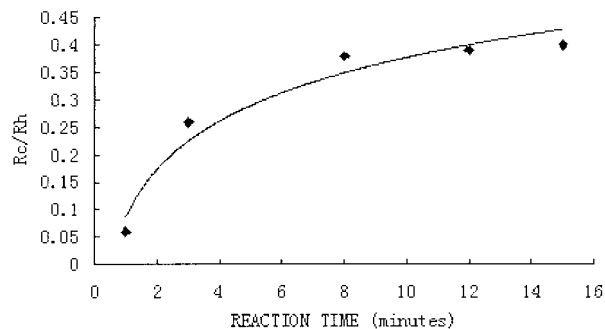


Figure 8 R_c/R_h of MMA with different reaction times. The chlorine contents: 61.7% Wt%; the amount of MMA: 20 parts.

formed from the mechanochemistry reaction of HCPE and MMA.

Further support for this hypothesis is provided by the NMR results. Changes in the integral at 3.63 ppm in the $^1\text{H-NMR}$ spectra of HCPE-g-MMA without PMMA were found with changes in the amount of MMA and reaction time, etc., again proving that MMA grafted onto HCPE by the mechanochemistry reaction.

Influence of amount of MMA on polymer structure

The amount of MMA added during the mechanochemistry reaction has an important effect on the polymer structure. A series of products was synthesized by adding amounts of MMA from 5 to 30 parts, and $^1\text{H-NMR}$ spectra of the samples were determined. Calculations of conversion, GD, GE, and R_c/R_h of HCPE-g-MMA versus the amount of MMA were calculated and the results are shown in Figures 3–5.

The increases in conversion and GD and the decrease in GE with increasing MMA content show that the amount of polymer increases continually and that the homopolymerizing rate has a quicker rise than the grafting rate. In other words, the greater the amount of MMA, the larger is the value of R_h , resulting in the decrease of R_c/R_h . Increasing the concentration of monomers is especially helpful in terms of forming PMMA, even though it is beneficial to producing HCPE-g-MMA copolymers.

Influence of mechanochemistry reaction time on polymer structure

The mechanochemistry reaction time is another important factor affecting polymer structure. HCPE, with chlorine content of 61.7%, was made with 20 parts of MMA by mechanochemistry reactions of different reaction times. $^1\text{H-NMR}$ spectra of the samples were determined. Conversion, GD, GE, and R_c/R_h of HCPE-g-MMA were calculated and the results are shown in Figure 6–8. The results indicate that conversion, GD, GE, and R_c/R_h of the material all rise grad-

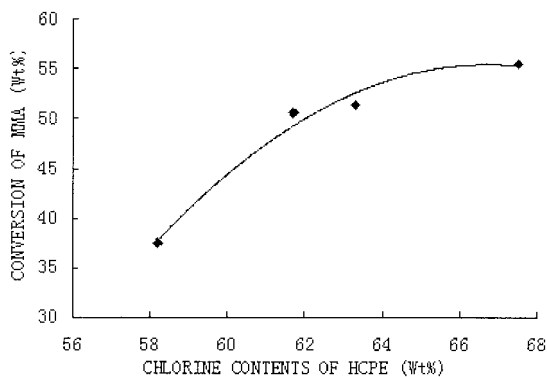


Figure 9 Conversion of MMA with various chlorine contents of HCPE. Reaction time 15 minutes; the amount of MMA: 20 parts.

ually with reaction time to a stable value after 8 min. The concentration of MMA in the system drops continually with the reaction time and, after 8 min, the amount of the monomer is so low that the polymerization stops.

Effect of chlorine contents on polymer structure

The chlorine content of the HCPE defines the HCPE-g-MMA structure because the reaction degree is dependent on the intensity of shear stress in the mechanochemistry reaction. In this reaction, the higher the chlorine content of HCPE, the larger is the shear stress that the material undergoes from the two-roll mill and the more easily are the HCPE molecules broken up to form free radicals. This series of events explains the changes in conversion, GD, GE, and R_c/R_h that occur with varying the chlorine content of HCPE.

The $^1\text{H-NMR}$ spectra of HCPE-g-MMA with different chlorine contents were determined and used to calculate conversion, GD, GE, and R_c/R_h values for HCPE-g-MMA. The results are as shown in Figures 9–11. Conversion, GD, GE, and R_c/R_h all increased with the increase of chlorine content of HCPE. The

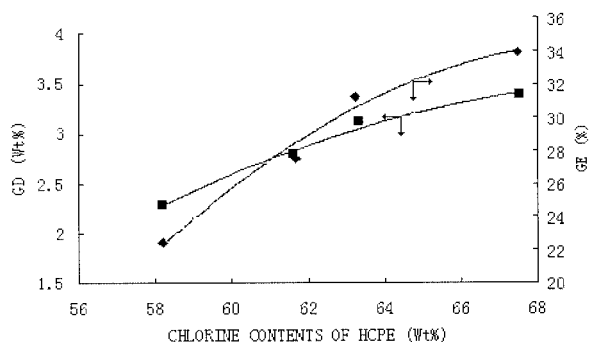


Figure 10 GD and GE of MMA with various chlorine contents of HCPE. Reaction time 15 minutes; the amount of MMA: 20 parts.

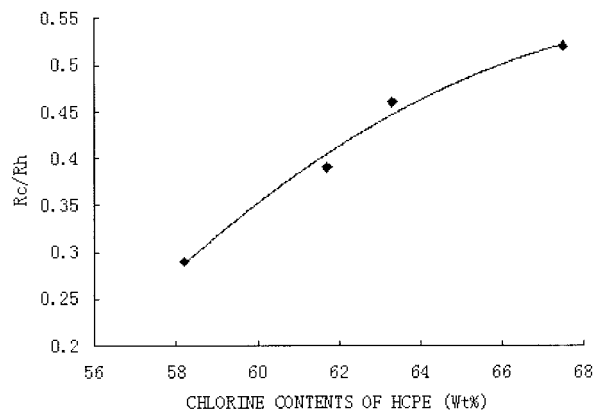


Figure 11 R_c/R_h of MMA with various chlorine contents of HCPE. Reaction time 15 minutes; the amount of MMA: 20 parts.

tendency is to favor grafted copolymerization.

The results of this study show that the GD and GE values for MMA grafted onto HCPE by the mechanochemistry reaction are all more than those for MMA grafted onto HCPE by the grafting reaction in a water phase.⁵ The mechanochemistry reaction is, therefore, more favorable for the generation of grafted copolymers.

CONCLUSIONS

The results of this study indicate the following:

1. Grafting of MMA onto HCPE can be attained by the mechanochemistry reaction in a two-roll mill.
2. With increasing amount of MMA in the system, conversion and GD increase, but GE decreases gradually, indicating that an increase of MMA content favors formation of homopolymer.
3. After a reaction time of 8 min, conversion, GD, GE, and R_c/R_h essentially reach maximum values and then do not change significantly even if the reaction time is extended.
4. The effect of chlorine content of HCPE on HCPE-g-MMA structure is very obvious; that is, conversion, GD, GE, and R_c/R_h all increased with an increase of chlorine content.

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