

## Iodoform-Mediated Free Radical Emulsion Polymerization of Chloroprene

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**ABSTRACT:** The free radical emulsion polymerization of chloroprene (CP) is carried out at 9°C using different amounts of iodoform as the chain transfer agent. The molecular weight of polychloroprene (PCP) can be regulated effectively by CHI<sub>3</sub>. PCP suitable for use as an adhesive is obtained with 0.22–0.28 wt % CHI<sub>3</sub> and reaches even higher monomer conversion than when mercaptan is used as the chain transfer agent. The emulsion polymerization of CP with high amounts of CHI<sub>3</sub> (1.0–3.0 wt %) proceeds in a living polymerization manner. The molecular weight increases in proportion to the monomer conversion in the range of the whole polymerization process even up to very high monomer conversion. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** emulsion polymerization; radical polymerization; living polymerization; chain transfer agent; polychloroprene

Received 26 July 2011; accepted 17 May 2012; published online

DOI: 10.1002/app.38082

### INTRODUCTION

Recent advancements in controlled radical polymerization (CRP), particularly nitroxide-mediated radical polymerization (NMRP),<sup>1,2</sup> atom transfer radical polymerization (ATRP),<sup>3,4</sup> and reversible addition-fragmentation chain transfer polymerization (RAFT),<sup>5</sup> have provided a new method for the preparation of well-defined polymers. Iodide-mediated radical polymerization was discovered by Tatemoto and coworkers.<sup>6</sup> The degenerative transfer (DT) mechanism involved in this type of polymerization was first proposed by Matyjaszewski et al.<sup>7–9</sup> and was investigated in detail by Fukuda et al.<sup>10</sup> In DT mechanism, a conventional radical initiator and a specific iodine-containing transfer agent are needed. A great advantage of the reversible transfer technique in iodide-mediated living radical polymerization is that experimental conditions, such as temperature, concentrations, processes, among others, can be made very close to conventional conditions. Furthermore, metal catalysts as in ATRP or expensive reagents as in NMRP and RAFT are eliminated in the iodide-mediated radical polymerization, and therefore, no need to remove or reclaim them after the completion of the polymerization. Many block and star polymers have been synthesized using iodide-mediated radical polymerizations involving bulk, solution, and mini-emulsion systems.<sup>7,11–15</sup> In our study, amphiphilic block and star copolymers were prepared using this controlled method.<sup>16,17</sup>

Although many monomers have been polymerized successfully using various living radical polymerizations and many kinds of

polymers or copolymers have been prepared with well-defined structures, the research on controlled radical (co) polymerization of 1,3-diene monomers was seldom reported probably because of the lower propagating constant ( $k_p$ ) of 1,3-diene monomers. The polymerization rate of most controlled free radical polymerizations is lower than that of conventional radical polymerization because of the low concentration of free radicals. In addition, the higher polymerization temperature of CRP for diene monomers compared with that in industrial production of 1,3-diene rubbers is another disadvantage. For example, NMRP of isoprene and butadiene has been carried out at 120–130°C<sup>18,19</sup>; ATRP of butadiene has been investigated at 110–130°C<sup>20</sup>; and RAFT polymerization of isoprene has been performed at 70°C.<sup>21,22</sup> The traditional production methods of butadiene–styrene rubber (SBR) and butadiene–acrylonitrile rubber (NBR) employ low-temperature technology (at 5°C and 5–15°C, respectively) and high-temperature technology (at 50°C and 30–50°C, respectively). Low-temperature technology is used extensively in the industry. Polymerizations at high temperatures tend to generate 1,3-diene (co)polymer with a microstructure unsuitable for commercial uses. Fortunately, chloroprene (CP) has a much higher propagating rate constant than butadiene and isoprene due to the chlorine atom at its 2-position. Therefore, CRP of CP may be carried out at low temperatures similar to the technology commonly used in industrial production. Polychloroprene (PCP) is generally produced using emulsion polymerization either at lower temperatures ( $\leq 20^\circ\text{C}$ ) or at higher temperatures (about 40°C). Xanthogen disulfide<sup>23</sup> or

mercaptan<sup>24,25</sup> is generally used as a conventional chain transfer agent in the emulsion polymerization of CP to regulate molecular weight. Traditional CP polymerization does not proceed in a controlled fashion. Therefore, precisely controlling the molecular weight of PCP is difficult.

In this article, emulsion polymerization of CP was carried out at 9°C using iodoform as the chain transfer agent. The molecular weight of PCP can be regulated effectively by the amount of iodoform and monomer conversion. The emulsion polymerization of CP proceeded in a controlled fashion. To the best of our knowledge, this is the first report on controlled free-radical emulsion polymerization of CP. Moreover, the prepared PCP with 0.22–0.28 wt % CHI<sub>3</sub> exhibited the same properties as the commercial products. CHI<sub>3</sub> might have potential as a novel molecular weight regulator to displace odorous mercaptan in the emulsion polymerization of CP.

## EXPERIMENTAL

### Materials

CP, emulsifiers [disproportionated rosin, sodium dodecyl sulfate, Lomar PW (condensation product of sodium naphthalene-sulfonate and formaldehyde)], redox initiator (potassium persulfate, sodium sulfite, sodium formamidine sulfinate), terminating agents (phenothiazine and antioxidant-264), sodium hydroxide, sodium carbonate, and methanol were all provided by Shanxi Synthetic Rubber Group Co. (Datong, China) and used without further purification. Iodoform (>99%, Tianjin Fuchen Chemical Reagent Factory) wrapped in silver paper was stored in a dark place and used directly without further treatment. All other materials were chemically pure agents which did not undergo further purification.

### Emulsion Polymerization of CP

Disproportionated rosin (26.6 g) and iodoform (0.20–0.30% and 1.0–3.0% of monomer, wt., respectively) were dissolved in CP (700 g, 7.9 mol) to prepare the oil phase. All other components (1.4 g, 4.85 mmol sodium dodecyl sulfate; 2.8 g Lomar PW; 5.1 g, 0.13 mol NaOH; and 1.4 g, 13.2 mmol Na<sub>2</sub>CO<sub>3</sub>), except the redox initiator, were dissolved in deionized water (770 mL) to prepare the aqueous phase. Then, the aqueous mixture was poured into the oil phase while stirring at about 20°C. After stirring for 35 min, the emulsion obtained was cooled to 9°C. Potassium persulfate (1.75 g, 6.47 mmol), sodium sulfite (1.05 g, 8.33 mmol), and sodium formamidine sulfinate (1.05 g, 12.19 mmol) aqueous solutions (total water 210 mL) were then added successively. The polymerization was carried out at 9 ± 1°C. At definite time intervals, portions of the latex sample were withdrawn to determine the monomer conversion. The samples for molecular weight and Mooney viscosity measurements were obtained by coagulating the emulsion in a large amount of cold methanol after terminating the polymerization with the terminating agent emulsion containing 14 g antioxidant-264, 0.35 g phenothiazine, 7 g ordinary rosin, 1.05 g NaOH, 49 mL toluene, and 70 mL water.

### Characterization

Monomer conversion in the emulsion polymerization of CP was obtained by determining the latex gravity because it has been

demonstrated that the latex gravity of CP was in proportion to monomer conversion.<sup>26</sup> Mooney viscosity of PCP rubber was determined on ZND-1 Automatic Mooney Viscosity Instrument according to ZBG35001-88. Peel strength, volatile content and ash content were determined according to ZBG35001-88. The number-average molecular weights and molecular weight distributions of PCP were determined using Gel Permeation Chromatography (GPC). When the dosage of CHI<sub>3</sub> was less (CHI<sub>3</sub>/CP ≤ 0.30% wt.), Waters HPLC-515 GPC was used, which was equipped with three chromatographic columns (Styragel HT6E, Styragel HT5, and Styragel HT3), and a Waters 2410 differential refractometer detector. When the dosage of CHI<sub>3</sub> was relatively high (CHI<sub>3</sub>/CP ≥ 1.0% wt.), TOSOH HLC-8220 GPC was used, which had two chromatographic columns (TSKgel SuperMulti-pore HZM-M × 2) in order to reach high resolution and accuracy. The eluent of both GPC was THF (40°C), with flow rates of 1 and 0.35 mL/min, respectively. The polystyrene standards with narrow molecular weight distributions were used to generate the calibration curves. <sup>1</sup>H-NMR spectra were recorded on a Bruker AV600-MHz NMR spectrometer at room temperature with CDCl<sub>3</sub> as the solvent.

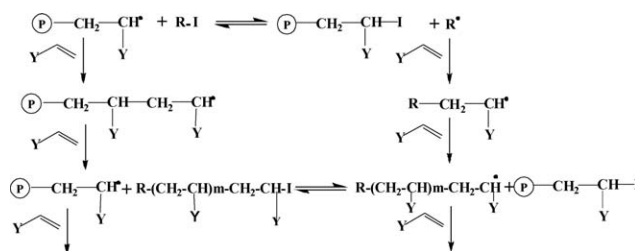
## RESULTS AND DISCUSSION

In the emulsion polymerization of synthetic rubber, such as butadiene–styrene rubber, butadiene–acrylonitrile rubber, CP rubber, mercaptan is usually used as the chain transfer agent to regulate the molecular weight of the polymer and to restrain cross-linking from diene monomers.<sup>24,25</sup> The polymerization must be stopped because the concentration of mercaptan decreases with an increase in the monomer conversion, reaching ~ 65–70%. Otherwise, insoluble gel would be formed and the properties of the rubber would not meet the requirements in practical applications.

According to DT mechanism shown in Scheme 1, if the appropriate iodocompounds are used as the chain transfer agent in the emulsion polymerization of diene monomers, the content of the chain transfer agents (micromolecule iodocompounds in the earlier stage and macromolecule iodocompounds in the later stage) would remain constant during the whole polymerization process. Consequently, the molecular weight of the polymer could be controlled effectively even when monomer conversion is much higher.

### Emulsion Polymerization of CP with 0.20–0.30 wt % CHI<sub>3</sub> as Chain Transfer Agent

In this study, CHI<sub>3</sub> was chosen as the chain transfer agent in the emulsion polymerization of CP because it is commercially



Scheme 1. DT mechanism of iodocompounds.

**Table I.** Effects of the Amount of CHI<sub>3</sub> on the Properties of PCP

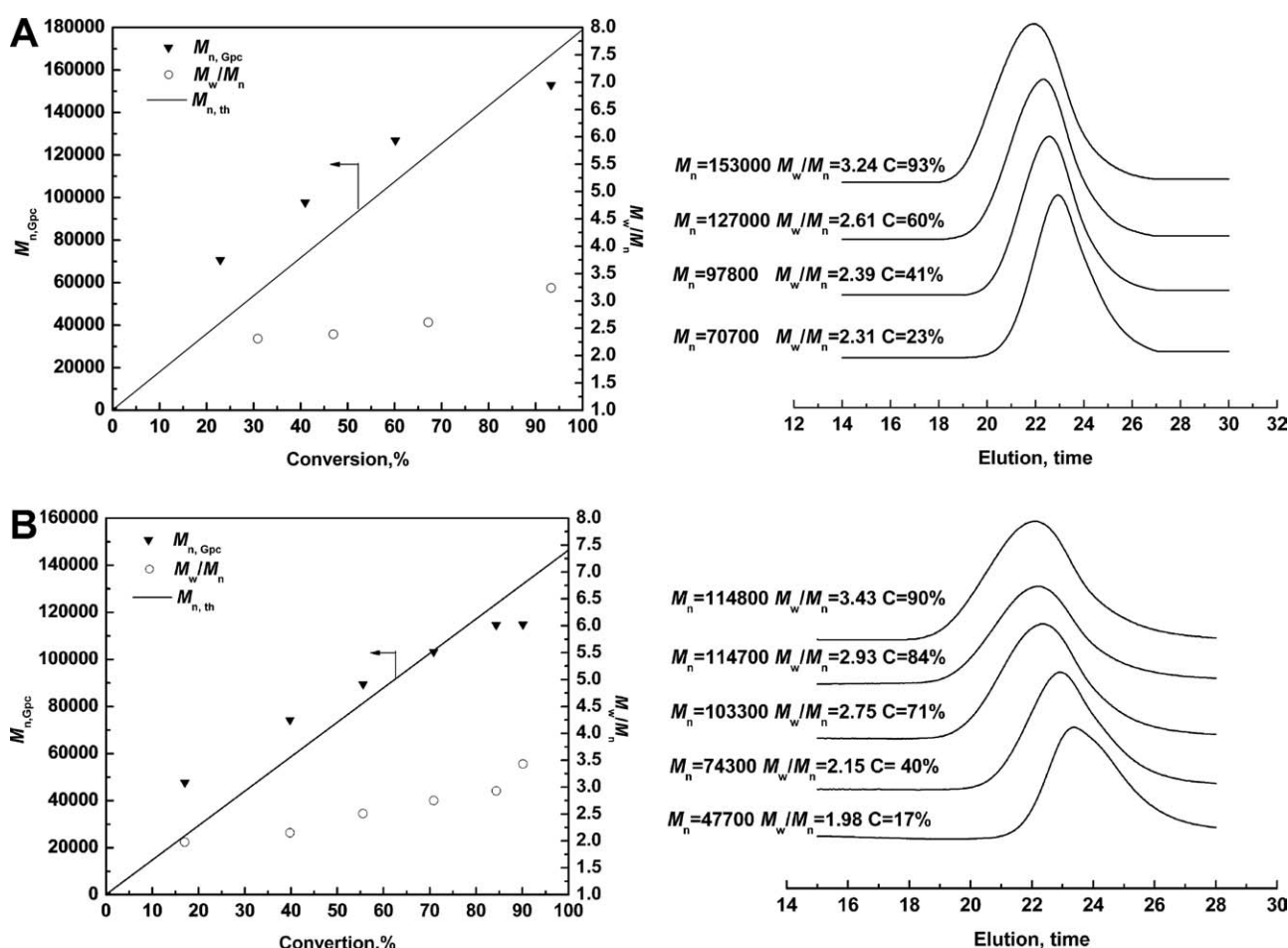
CHI <sub>3</sub> (wt %)	Latex gravity (g/cm <sup>3</sup> )	Monomer conversion (%)	Mooney viscosity (ML <sub>2+2.5</sub> <sup>100°C</sup> )	Peel strength (MPa)	Volatile content/ash content (%)
0.22	1.081	93	49	87	1.0/1.0
	1.082	94	52	90	1.0/1.0
0.25	1.082	94	40	98	1.0/1.1
	1.082	94	47	107	-
0.28	1.082	94	39	94	1.1/1.0
	1.082	94	41	99	1.1/1.0
0.30	1.082	94	38	-	-

available. CHI<sub>3</sub> has also been used in CRP of styrene and acrylate.<sup>16</sup>

When the amount of CHI<sub>3</sub> was lower than 0.15%, the Mooney viscosity (ML<sub>2+2.5</sub><sup>100°C</sup>) of PCP was higher than 100 and insoluble gel in the products were formed. When the amount of CHI<sub>3</sub> was between 0.22 and 0.30%, PCPs with proper Mooney viscosity suitable for adhesive (ML<sub>2+2.5</sub><sup>100°C</sup> in the range of 35–55) were obtained (Table I). Other performance parameters, such as

peel strength and volatile content/ash content, were all in the range of the commercial products.<sup>27</sup> Furthermore, higher monomer conversion (>90%) could be achieved with CHI<sub>3</sub> than with mercaptan as the chain transfer agent (Table I).

Figure 1 shows the number-average molecular weights ( $M_n$ ), polydispersity indexes ( $M_w/M_n$ ), and molecular weight distribution curves of the PCPs obtained at different monomer conversions when 0.22 and 0.28% of iodoform were used.



**Figure 1.**  $M_n$ ,  $M_w/M_n$ , and molecular weight distribution curves of PCPs obtained at different monomer conversions. Concentration of CHI<sub>3</sub>: (A) 0.22% and (B) 0.28%.

If the polymerization proceeds according to the DT mechanism proposed by Matyjaszewski et al.,<sup>7–9</sup> the theoretical number-average molecular weights ( $M_{n, th}$ ) of the polymers can be calculated according to eq. (1):

$$M_{n, th} = \Delta[CP]/[CHI_3] \times M_{CP} + M_{CHI_3} \quad (1)$$

where  $\Delta[CP]$  is the amount of monomer polymerized,  $[CHI_3]$  is the amount of  $CHI_3$  added,  $M_{CP}$  is the molecular weight of CP and  $M_{CHI_3}$  is the molecular weight of  $CHI_3$ . Figure 1 shows that the number-average molecular weight of PCP increased with monomer conversion. Under similar monomer conversion, the higher the concentration of  $CHI_3$ , the lower the number-average molecular weight. Furthermore, the molecular weight distribution curves were all unimodal within the range of the whole polymerization process. These results show that the emulsion polymerization of CP at 9°C with  $CHI_3$  as the chain transfer agent exhibited the characteristics of controlled free-radical polymerization. As a result, the molecular weight of PCP can be controlled by the amount of chain transfer agent and monomer conversion. According to DT radical polymerization mechanism, the content of the chain transfer agents,  $CHI_3$  in the early stage and PCP-I in the later stage, remained constant during the whole polymerization process. Consequently, the conversion of CP can easily reach 90% or above with  $CHI_3$  as the chain transfer agent, whereas that in the presence of mercaptan was lower than 70%.

Some deviations from ideal living free-radical polymerization exist. Although the molecular weight distribution was narrower than commercial PCP (the molecular weight distribution is between 2.5 and 3.0), it was broader than that of polystyrene prepared with  $CHI_3$ , specifically at higher monomer conversions.<sup>8,9</sup> Fortunately, although the molecular weight distributions of PCPs obtained in the presence of  $CHI_3$  were much broader than those obtained in living free-radical polymerization of other vinyl monomers, the commercial PCP does not need very narrow molecular weight distribution to obtain good property for its adhesive solution in toluene.<sup>28,29</sup> The contents of the emulsion polymerization of CP used in our study were the same as those used industrially, except that mercaptan or xanthogen disulfide was replaced with  $CHI_3$ . The polymerization rate in the presence of  $CHI_3$  was also similar to the rate elicited by xanthogen disulfide as the chain transfer agent. The combination of the sharp increase in the final monomer conversion regulated by  $CHI_3$  and the rapid polymerization rate in the conventional emulsion polymerization would likely cause great economic repercussions in the production of PCP.

The relatively broader weight distribution was probably caused by the low concentration of  $CHI_3$  relative to the redox initiator and low diffusion rate of  $CHI_3$  from monomer droplets to latex particles in the emulsion polymerization system. Another contribution to the high polydispersity index may arise from the branching of PCP formed by the transfer reaction to macromolecule or addition reaction to the vinyl bond of the macromolecule of the radicals because various addition patterns and isomerized units of CP were observed.<sup>30</sup> In addition, branching could not be avoided in radical (co)polymerization of 1,3-diene

monomers and would be serious when monomer conversion is high in conventional radical polymerization. Branching due to chain transfer and subsequent combination, among others, may also be present in our experiment and could become serious with the increase in monomer conversion. Therefore, the polydispersity index increases with monomer conversion.

### Emulsion Polymerization of CP with 1.0–3.0 wt % $CHI_3$ as Chain Transfer Agent

The polymerization was carried out under larger concentrations of  $CHI_3$  to further confirm that the emulsion polymerization of CP with  $CHI_3$  as the chain transfer agent indeed proceeded in a controlled polymerization manner. The results are shown in Figure 2.

The results further prove that the emulsion polymerization of CP in the presence of  $CHI_3$  indeed exhibited some characteristics of living free-radical polymerization. For example, the number-average molecular weight of PCP increased with the increase in monomer conversion. Under similar monomer conversions, the higher the  $CHI_3$  concentration, the smaller the number-average molecular weight. Furthermore, with an increase in the  $CHI_3$  concentration, the molecular weight distribution became gradually narrower. When the  $CHI_3$  concentration reached 3.0% of CP (wt.), the polydispersity indexes were always lower than 2.5 in the range of the whole polymerization process, including those at very high monomer conversion (>90%). Furthermore, even if the  $CHI_3$  concentration was reduced to 0.20–0.30 wt %, which was chosen for preparing the PCP rubber with much higher molecular weights, the polydispersity indexes were still less than 3.4 (Figure 1) during the whole process of up to more than 90% monomer conversion.

### <sup>1</sup>H-NMR Spectrum of PCP Prepared with $CHI_3$ as Chain Transfer Agent

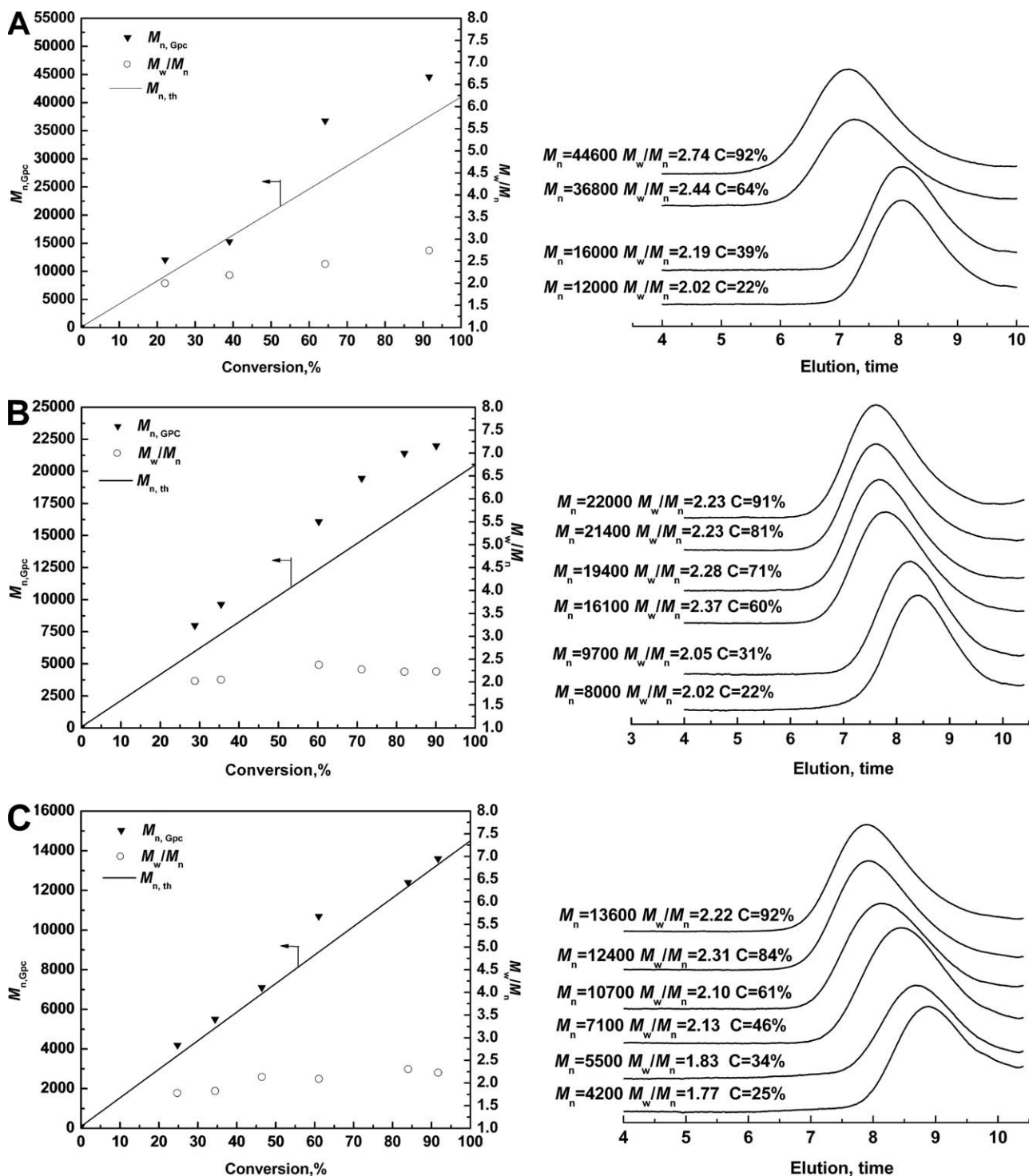
According to the mechanism proposed by Matyjaszewski et al.,<sup>7–9</sup> the PCP prepared above should have the molecular structure shown in Figure 3. In the <sup>1</sup>H-NMR spectrum of PCP, in addition to the signals between 5 and 6 ppm (peaks *c*) ascribed to the CP repeating units, characteristic signals originating from the  $\alpha$ -end and  $\omega$ -end groups, namely, peaks *a* and *b* around 4.54 and 4.68 ppm for the protons of the transfer agent moiety and the methine proton adjacent to the  $\omega$ -end iodine, were observed.

The number molecular weight of PCP can be calculated according to eq. (2):

$$M_{n, NMR} = (3 \times I_c / I_{a+b}) \times M_{CP} + M_{CHI_3} \quad (2)$$

where  $I_c$  and  $I_{a+b}$  are the integral values of the peaks at *c* and *a* with *b*, respectively. The calculated  $M_{n, NMR}$  was 2500, which was close to the theoretical value (2370) according to the monomer conversion and feed ratio. Similarly,  $M_{n, NMR}$  of PCP sample prepared with 2.0 wt %  $CHI_3$  when the monomer conversion was 16% was calculated to be 3300, which was also close to the theoretical value (3160). These results indicate that the polymerization of CP in the presence of  $CHI_3$  proceeds according to the DT radical polymerization mechanism.



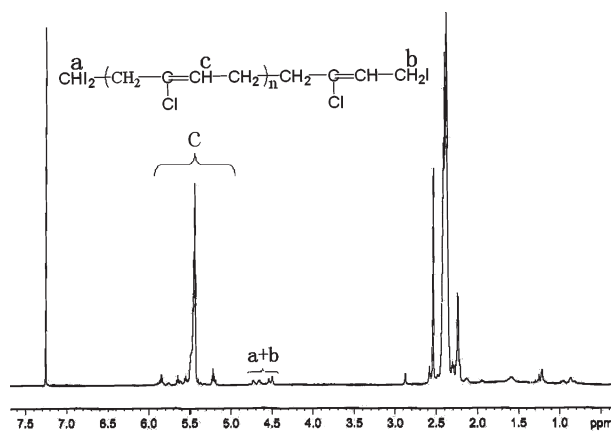


**Figure 2.**  $M_n$ ,  $M_w/M_n$ , and molecular weight distribution curves of PCP obtained at different monomer conversions with various amount of  $\text{CHI}_3$ . Concentration of  $\text{CHI}_3$ : (A) 1.0%, (B) 2.0%, and (C) 3.0%.

If every PCP macromolecule chain possesses an iodine atom at the  $\omega$ -end, they should be able to act as the macrochain transfer agent in the polymerization of the second monomer, so block copolymers are generated. The study on the synthesis of block copolymers is underway in our laboratory.

## CONCLUSIONS

The emulsion polymerization of CP with 0.22–0.28 wt %  $\text{CHI}_3$  as the chain transfer agent at 9°C could produce PCP adhesive with proper Mooney viscosity and peel strength, even when the monomer conversion was higher than 90%.  $\text{CHI}_3$  might have



**Figure 3.**  $^1\text{H-NMR}$  spectrum of PCP prepared with  $\text{CHI}_3$  as the chain transfer agent. Reaction condition:  $[\text{M}]_0 = 4.52\text{M}$ ;  $\text{CHI}_3/\text{CP} = 3.0$  wt %;  $[\text{M}]_0 : [\text{CHI}_3]_0 : [\text{K}_2\text{S}_2\text{O}_8]_0 = 1220 : 8.2 : 1$ ; temperature,  $9^\circ\text{C}$ , monomer conversion, 18%;  $M_n, \text{GPC} = 3000$ ,  $M_w/M_n = 1.63$ .

potential as a novel molecular weight regulator to replace the ordous mercaptan in the emulsion polymerization of CP.

The emulsion polymerization of CP with a higher amount of  $\text{CHI}_3$  (1.0–3.0 wt %) as the chain transfer agent proceeded in a controlled fashion. The molecular weight of PCP increased in proportion to the monomer conversion in the range of the whole polymerization process, even with very high monomer conversion (>90%). The polymerization kinetics was interpreted according to the DT radical polymerization mechanism.

#### ACKNOWLEDGMENTS

This work was subsidized by the National Natural Science Foundation of China (51073010). The authors acknowledge the GPC support of this work from Tosoh Corporation of Japan.

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