

Preparation and Application of Low Molecular Weight Poly(vinyl chloride). I. Preparation and Thermal Stability

KIKUO YAMAMOTO,* TAKASHI MAEHARA, KATSUO MITANI, and YUKIO MIZUTANI

Tokuyama Soda Co., Ltd., Mikage-cho, Tokuyama-city, Yamaguchi, 745 Japan

SYNOPSIS

Poly(vinyl chloride) with relatively low molecular weight (LMW-PVC) was prepared by suspension polymerization in the presence of some chain-transfer agents, such as mercapto compounds. It is elucidated by means of thermogravimetry, dehydrochlorination, color difference, and discoloration that the resultant LMW-PVC has good thermal stability. The degree of dehydrochlorination of the LMW-PVC obtained by using *n*-dodecylmercaptan increases with increasing the content of component from the chain-transfer agent. It is found that the LMW-PVC obtained by using mercapto compounds shows better thermal stability (discoloration property) than does the one obtained without using these agents, at the same weight-average polymerization degree. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl chloride) (PVC) has some excellent properties including mechanical strength and chemical resistance but has some serious defects: poor processability and inferior stability to heat and light. Thermal decomposition of PVC is occurs mainly due to dehydrochlorination during molding and practical use.¹

Generally, PVC with relatively low molecular weight (LMW-PVC) with lower melt viscosity has good miscibility for PVC with relatively higher molecular weight (HMW-PVC). It is well known that LMW-PVC can be produced by polymerization at relatively higher polymerization temperature² or in the presence of chain-transfer agents.³⁻⁵ Moreover, Zhan et al.⁶ studied the chain-transfer effect of different chain-transfer agents (mercaptoethanol, *n*-dodecylmercaptan) during polymerization of vinyl chloride (VC).

However, Abbas et al.⁷ and other authors⁸ showed that the total labile chlorine atoms increases with decreasing molecular weight of PVC. LMW-PVC has poor thermal stability (dehydrochlorination re-

action, discoloration time) compared with that of HMW-PVC.⁹⁻¹²

We investigated the preparation and thermal stability of LMW-PVC obtained by suspension polymerization in the presence of some chain-transfer agents and found that some mercapto compounds are effective chain-transfer agents that improve thermal stability.

EXPERIMENTAL

Materials

Vinyl chloride (VC) and other chemicals were of commercial grade. HMW-PVC was of commercial grade prepared by suspension polymerization (Grade: SUNAR 1000D, weight-average polymerization degree [P_w] = 1020 (Sun Arrow Chemical Co., Japan)).

Polymerization

LMW-PVC samples were prepared by suspension polymerization as follows: A stainless-steel autoclave (10 L) was charged with 5 kg of deionized water, into which 6 g of partially saponified poly(vinyl alcohol) (PVA) (degree of saponification, 80%), 3 g of methyl cellulose (MC), and definite amounts of the chain-transfer agent and *t*-butylperpivalate were

* To whom correspondence should be addressed at the Sun Arrow Chemical Co., Ltd., 1-2 Halumi-cho, Tokuyama-City, Yamaguchi, 745 Japan.

added. The autoclave was evacuated, and VC was fed into it and polymerized at 60°C for 3–4 h with stirring. The resultant PVC was washed with methanol and then dried under reduced pressure at 40°C.

Characterization of LMW-PVC

The weight-average polymerization degree (P_w) was determined according to JIS K-6721. The molecular weight distribution (M_w/M_n) was measured at 23°C in tetrahydrofuran solution using gel permeation chromatography (Type-200 from Waters Co.).

Compounding

LMW-PVC (100 parts) were mixed with tribasic lead sulfate (1 part) as a stabilizer and calcium stearate (1 part) and stearic acid as a lubricant (0.2 parts) in a Henschel mixer. The resultant mixture was milled at 170°C for 5 min using a mill with two mixing rollers to produce sheets (1 mm thick) for the discoloration test.

Thermal Stability Behavior

Thermogravimetric data were obtained in air using 15 mg of the sample using a thermogravimetric analyzer, type PTC-10A from Rigaku Denki Co. The heating rate was 10°C/min. Dehydrochlorination reactions^{12,13} were carried out under a nitrogen stream at 180°C using 100 mg of the LMW-PVC samples.

Hydrogen chloride was collected in 50 mL of water (25°C) and determined by electric conductometry.¹⁴ The degree of dehydrochlorination (\times mol/

mol-VC) was determined as the molar ratio between the mol of hydrogen chloride evolved and the mol of VC in PVC used.

Color Difference

A roll-milled sheet was set in an air oven at 180°C for 30 min and then the discoloration of the sheet was measured with a color difference meter, type DN-K5 from Nippon Denshoku Kogyo Co. Thus, the lightness index (L) and the chromaticness index (a, b) were estimated. The color difference of the sheet (ΔE) was calculated by the Hunter color difference equation:

$$\Delta E(\text{NBS}) = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2}$$

Here, L , a , and b are the values of the MgO plate as the standard: $L = 90.8$, $a = 0.4$, and $b = 4.0$.

Discoloration Time

Test pieces (3 × 5 × 0.1 cm) were set on aluminum foil and aged in a circulating air-oven at 180°C. Discoloration time was determined as the time elapsing until the samples turned completely black.

RESULTS AND DISCUSSION

Table I shows the results of the preparation and some characteristics of HMW-PVC and LMW-PVC. HMW-PVC (No. 1) and LMW-PVC (Nos. 2

Table I Synthesis of LMW-PVC

Sample No.	Chain-transfer Agent (mol/mol-VC) × 10	Temperature (°C)	Time (h)	Yields (%)	P_w
1	—	60	3.5	72.8	830
2	—	70	3.5	78.8	580
3	—	80	2.5	75.0	470
4	BMC 0.64	60	3.0	62.5	480
5	OMC 0.64	60	3.0	67.2	360
6	DMC 0.13	60	3.0	69.3	460
7	MCH 0.37	60	3.0	36.9	420
8	MET 0.13	60	3.0	61.9	469
9	MIZ 0.24	60	3.0	13.9	530
10	TGR 0.25	60	3.0	69.1	535
11	BTP 0.41	60	3.0	23.6	470

VC: 7.5 mol/L H₂O. Polymerization initiator: *t*-butylperpivalate, 0.04 mol/L-VC. BMC: *n*-butylmercaptan; OMC: *n*-octylmercaptan; DMC: dodecylmercaptan; MCH: mercaptocyclohexan; MET: 2-mercaptoethanol; MIZ: mercaptoimidazole; TGR: α -thioglycerol; BTP: *t*-butyl thiophenol.

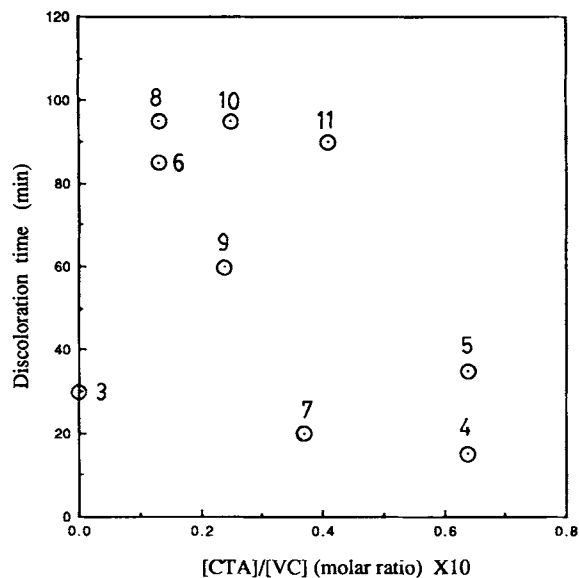


Figure 1 Relationship between discoloration time and molar ratio of some chain-transfer agents.

and 3) were prepared without chain-transfer agents (at different higher temperatures). LMW-PVC (Nos. 4–11) were prepared in the presence of various chain-transfer agents. The P_w of LMW-PVC (Nos. 4–11) are approximately 350–540.

The color difference (ΔE) of LMW-PVC (No. 5) is larger than that of the other LMW-PVC, and LMW-PVC (No. 9) has the smallest ΔE of the LMW-PVC samples.

Discoloration time of LMW-PVC (Nos. 1–3) decreases with increasing polymerization temperature. On the other hand, the discoloration time of LMW-PVC (Nos. 6, 8, and 10) is improved compared with that of other LMW-PVC (Nos. 4, 5, 7, 9, and 11).

Furthermore, LMW-PVC obtained using the mercapto compound, except for LMW-PVC ob-

tained using *n*-butyl mercaptan (BMC) and mercaptocyclohexane (MCH), increases in comparison with LMW-PVC (No. 1). Hence, discoloration time (Nos. 4–6) obtained using alkyl mercapto compounds increases with increasing the carbon number of the alkyl group (*n*-butyl, *n*-octyl, and dodecyl), as shown in Table I.

Figure 1 shows the relation of the discoloration time to the molar ratio of the chain-transfer agents to VC. The discoloration time of LMW-PVC (Nos. 4–11) obtained using different mercapto compounds increases with decreasing molar ratio. The discoloration time of LMW-PVC obtained using *n*-dodecylmercaptan (DMC) and 2-mercaptoethanol (MET) shows better discoloration time than that of LMW-PVC (Nos. 2 and 3). Table II shows the result of LMW-PVC obtained using DMC and MET, which give good discoloration time, as shown in Table I, under various amounts of DMC and MET.

The LMW-PVC obtained using DMC had a P_w of 200–530 and an M_w/M_n of 2.6–3.3. The LMW-PVC obtained using MET had a P_w of 180–480 and an M_w/M_n of 2.2–6.9.

The P_w of LMW-PVC decreases with increasing molar ratio. The M_w/M_n of LMW-PVC obtained using DMC slightly changes with increasing molar ratio. On the other hand, the M_w/M_n of LMW-PVC obtained using MET drastically increases with increasing molar ratio.

Figure 2 shows thermogravimetric analysis curves for LMW-PVC (No. 1) and LMW-PVC (Nos. 12–14) obtained using DMC at the same polymerization temperature.

The weight loss of LMW-PVC (No. 1) by thermal decomposition gradually initiates from 230°C. The curves of Nos. 12–14 show that the weight loss initiates at about 210°C. Moreover, the weight loss of LMW-PVC increases with an increasing amount of DMC. These curves indicate that total weight loss

Table II Synthesis of LMW-PVC by Suspension Polymerization in the Presence of Mercapto Compounds

Sample No.	Mercapto Compounds (mol/mol-VC) $\times 10^2$	Time (h)	Yields (%)	P_w	M_w/M_n
12	DMC 0.55	3.5	79.4	530	2.6
13	DMC 2.90	3.5	71.6	320	3.1
14	DMC 14.40	4.0	44.5	200	3.3
15	MET 0.27	3.5	81.5	480	2.2
16	MET 0.96	3.5	36.0	260	3.1
17	MET 9.60	3.5	21.9	180	6.9

VC: 7.5 mol/mol- H_2O . Polymerization temperature: 60°C. Polymerization initiator: *t*-butylpervalate, 0.04 mol/L-VC.

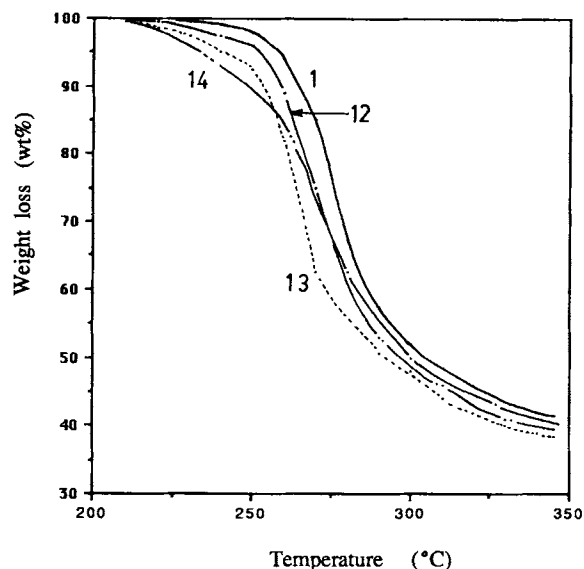


Figure 2 Thermogravimetric analysis of PVC obtained without chain-transfer agents and LMW-PVC obtained using DMC: (—) No. 1; (---) No. 12; (.....) No. 13; (- · - ·) No. 14.

is about 60% by weight and this value is approximately correspondent to the content of HCl in PVC (56.7%).

Figure 3 shows the time-dependency of the degree of dehydrochlorination of Nos. 1, 12, and 13 at 180°C. Until 70 min, the degree of dehydrochlorination increases with increasing P_w . Beyond 70 min,

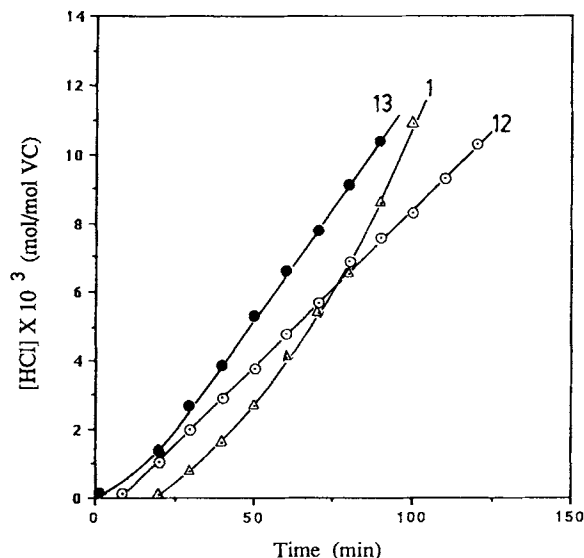


Figure 3 Thermal dehydrochlorination of PVC obtained without chain-transfer agents and LMW-PVC obtained using DMC: (Δ) No. 1; (\circ) No. 12; (\bullet) No. 13.

the degree of dehydrochlorination of LMW-PVC (No. 12) becomes slower than that of PVC (No. 1) with higher P_w . The dehydrochlorination reaction of LMW-PVC (No. 13) occurs without an induction period.

The thermal dehydrochlorination of PVC is related to the labile chlorine atoms. The total labile chlorine atoms of PVC increases with decreasing molecular weight.⁸ It is found that LMW-PVC (No. 12) shows better dehydrochlorination than that of No. 1 beyond about 75 min. Therefore, the dehydrochlorination reaction of LMW-PVC is affected by the P_w and molecular structure.

Figure 4 shows curves of discoloration time vs. $1/P_w$ of LMW-PVC sheets molded at 190°C. The discoloration time increases with increasing P_w in all cases.

It is well known that the thermal stability of PVC generally increases with increasing P_w . It is reasonable that the discoloration time of LMW-PVC obtained using a chain-transfer agent increases with increasing P_w . Figure 5 shows the relation of the discoloration time to the molar ratio of the chain-transfer agents to VC. The discoloration time of LMW-PVC obtained using different mercapto compounds increases with decreasing molar ratio.

Furthermore, it is found that the discoloration time of LMW-PVC obtained using DMC, MET, and

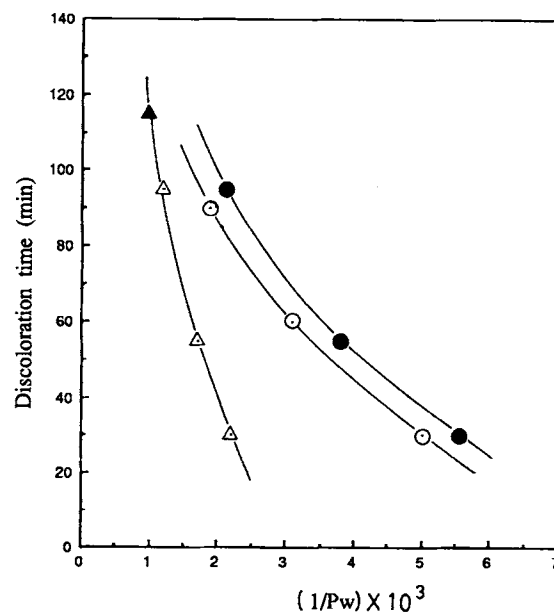


Figure 4 Relationship between discoloration time and $1/P_w$ of LMW-PVC obtained without chain-transfer agents and LMW-PVC obtained using DMC and MET: (\circ) DMC; (\bullet) MET; (Δ) no chain-transfer agent; (\blacktriangle) commercial PVC ($P_w = 1020$).

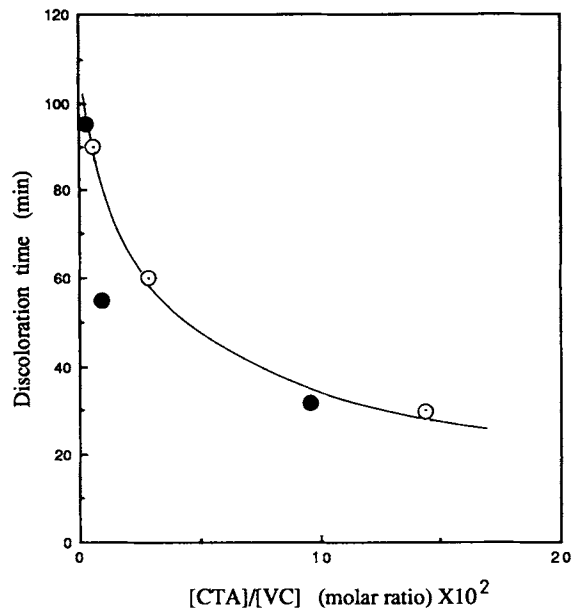


Figure 5 Relationship between discoloration time and molar ratio of chain-transfer agents: (○) DMC; (●) MET.

α -thioglycerol are improved more than that of the other mercapto compounds. The discoloration time is affected by the P_w of LMW-PVC and the kind of mercapto compounds. Therefore, it is concluded that the discoloration time of LMW-PVC obtained using mercapto compounds shows better discoloration time than the one obtained without using these agents (at higher polymerization temperature) at the same P_w .

CONCLUSION

LMW-PVC was prepared by suspension polymerization in the presence of some mercapto com-

pounds. The thermal stability of LMW-PVC was studied by estimating the thermal degradability, color difference, and discoloration time. At the same P_w , LMW-PVC obtained using mercapto compounds showed better thermal stability (discoloration time) than the one obtained without using these agents (at higher polymerization temperature).

REFERENCES

1. J. Imhof, W. Sshhanschula, and R. Haberleiyure, *J. Vinyl Technol.*, **1**, 47 (1979).
2. T. Y. Xue, A. E. Hamielec, P. E. Wood, and D. R. Woods, *J. Vinyl Technol.*, **13**, 2 (1991).
3. D. Lin and M. Kovinsky, *J. Polym. Sci.*, **53**, 173 (1961).
4. M. Langsam, *J. Appl. Polym. Sci.*, **23**, 867 (1979).
5. W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **61**, 1735 (1965).
6. Z. Xiaoli, W. Zhixue, H. Zhiming, and P. Zuren, *Chem. Abstr.*, **114**, 25214 (1991).
7. K. B. Abbas and E. M. Sorvic, *J. Appl. Polym. Sci.*, **20**, 2395 (1976).
8. M. Rogstedt and T. Hjetberg, *Macromolecules*, **25**, 6332 (1992).
9. B. Ivan, *J. Polym. Sci. Polym. Chem. Ed.*, **221**, 2177 (1983).
10. T. Hjetberg, *Polymer*, **24**, 685 (1983).
11. P. Xu, D. Zhou, and D. Zhao, *Eur. Polym. J.*, **26**, 581 (1989).
12. K. Patel, A. Velazquez, H. S. Calderon, and G. R. Brown, *J. Appl. Polym. Sci.*, **46**, 179 (1992).
13. B. B. Troitskii and L. S. Troitskaya, *J. Polym. Sci. Part A Polym. Chem.*, **31**, 75 (1993).
14. J. Millan, E. L. Mdruga, and G. Martinez, *Angew. Makromol. Chem.*, **45**, 177 (1975).

Received March 8, 1993

Accepted July 17, 1993