

Copolymerization of Vinyl Chloride with *trans*-1,2-Dichloroethylene

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Synopsis

Copolymerization of vinyl chloride with *trans*-1,2-dichloroethylene was carried out at various temperatures, and the properties of the copolymers obtained by the emulsion copolymerization at low temperature were examined. In the case of bulk copolymerization at temperatures higher than room temperature, the rate of polymerization, the equilibrium conversion, and $[\eta]$ were lowered with increasing content of *trans*-1,2-dichloroethylene in the initial monomer mixture, but the T_g and softening point of the copolymers containing about 15% of 1,2-dichloroethylene unit were about 10°C. higher than these of conventional PVC resin, in spite of their inability to form films. The monomer reactivity ratios at 50°C. were 5.39 (VC) and 0.072 (*trans*-DCE). Emulsion copolymerization was carried out at -30°C. with the use of a redox initiator system (hydrogen peroxide-ferrous sulfate-ascorbic acid), in order to increase both the $[\eta]$ and the rate of polymerization. The copolymers prepared at low temperature had higher T_g and better solubility than the VC homopolymer polymerized at the same condition or conventional PVC resin. The results of the infrared absorption spectra, the solubilities, and the calculation of sequence length of VC monomer unit in the polymer chain indicated that the stereoregularity and the crystallinity of the low temperature copolymers were lower than those of the low temperature VC homopolymers. It was concluded that higher T_g and good solubility of the low temperature copolymer were brought about by the prevention of the free rotation of the polymer chain by the random distribution of 1,2-dichloroethylene units in the polymer chain.

INTRODUCTION

Copolymerization of vinyl chloride (VC) with *trans*-1,2-dichloroethylene (*trans*-DCE) was carried out at low temperatures, and properties of the copolymers obtained were examined.

It is well known that the homopolymerization of 1,2-disubstituted ethylenes takes place only with difficulty, in general, because of the steric hindrance of substituents. Copolymerization of 1,2-disubstituted ethylenes was carried out previously by several investigators,¹ and it was found that *trans*-DCE is more reactive toward styrene or vinyl acetate than *cis*-DCE. However, very little has been published on the copolymerization of DCE with VC.²

In the present study the emulsion copolymerization of VC with *trans*-DCE was carried out at low temperatures with a redox initiator system,

the results of the investigation of bulk copolymerization at high temperature were compared, and reactivity of monomers and properties of copolymers were investigated.

It was found that copolymers obtained by the emulsion copolymerization at low temperature had higher glass transition temperatures than VC homopolymers polymerized under the same experimental conditions and conventional poly(vinyl chloride) (PVC) resin and were soluble in tetrahydrofuran (THF) and cyclohexanone.

EXPERIMENTAL

Materials

Materials used, except VC monomer, were guaranteed reagent grade. VC monomer was purified by redistillation of the monomer, which was produced by Nippon Carbide Co.

Polymerization Procedure

Bulk Polymerization at High Temperature. Copolymerization was carried out at 20–50°C. under a nitrogen atmosphere. A glass ampule was charged with *trans*-DCE and azobisisobutyronitrile (AIBN) or lauroyl peroxide (LPO), cooled below –40°C. in a Dry Ice–methanol bath, and charged with VC. After flushing several times with oxygen-free nitrogen, the glass ampule was sealed off and set in a hot water bath. During the polymerization reaction, the reaction mixture in the ampule was not stirred. After several hours, the reaction mixture was dissolved in THF and the copolymer was precipitated with methanol. The white, powdery polymer obtained was filtered and dried at 50°C. in a vacuum dryer.

Emulsion Polymerization at Low Temperature. Emulsion polymerization was generally conducted at –30°C. in a stainless steel autoclave. The autoclave was cooled below –40°C. in a Dry Ice–methanol bath and charged with monomers, initiators, and other reagents in the following order: (1) mixture of water and methanol, containing ascorbic acid and emulsifier, (2) *trans*-DCE monomer, (3) aqueous solution of ferrous sulfate, (4) VC monomer, (5) hydrogen peroxide (30% aqueous solution). After charging, the autoclave was packed; and was flushed with oxygen-free nitrogen. The mixture was emulsified by vigorous stirring, and the polymerization was carried out at the given temperature with stirring. Several hours later, the reaction mixture was coagulated by addition of 20% aqueous calcium chloride, and the polymer obtained was filtrated with a glass filter, washed until no chlorine ion was detected in the wash water, and dried at 50°C. in a vacuum dryer.

Characterization of Polymer

The content of the DCE component in the copolymer was calculated from the chlorine content.³ The intrinsic viscosity $[\eta]$ was measured in

cyclohexanone solution at 30°C., and the degree of polymerization DP of VC homopolymer was calculated from eq. (1).⁴

$$DP = 500 \{ \log^{-1} ([\eta]/0.184) - 1 \} \quad (1)$$

The glass transition temperature T_g was determined dilatometrically with compression-molded sheet. The infrared absorption spectrum was obtained by the KBr disk method. The melt viscosity η_m was measured at 180°C. with the use of a KoKa flow tester having a 1 mm. diameter \times 10 mm. long orifice. The weight loss of the granulated polymer (about 100 mesh) was determined at 170°C. in an air bath.

RESULTS

Bulk Polymerization at High Temperature

The rates of polymerization at various monomer ratios of VC to *trans*-DCE at 50°C. are shown in Figure 1. In each case, the rate of polymerization, equilibrium conversion, and $[\eta]$ were lowered with increasing content of *trans*-DCE in monomer mixture. These results show that *trans*-DCE polymerization involves a chain transfer reaction, and it is presumed that the mechanism of chain transfer becomes more complicated, as is the case in the polymerization of styrene in *p*-deuteriodiethylbenzene,⁵ because *trans*-DCE is also introduced into the copolymer.

The chain transfer constant of VC is larger than that of other vinyl monomers.⁶ Moreover, the free radical $\text{CH}_2=\text{CH}\cdot$ produced by the chain

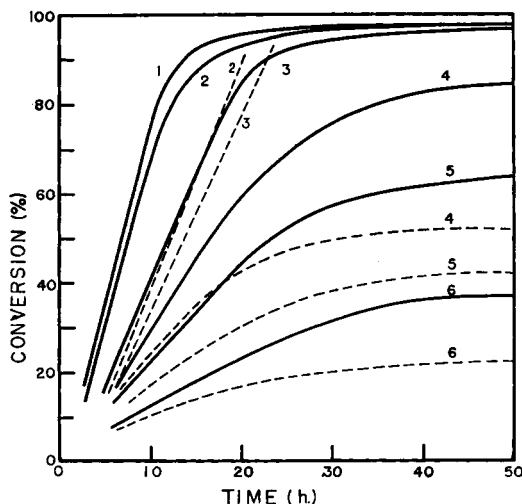


Fig. 1. Conversion vs. time curve for bulk copolymerization of VC and DCE at various initial monomer mixture compositions: (1) 100 mole-% of VC; (2) 90 mole-% of VC; (3) 80 mole-% of VC; (4) 70 mole-% of VC; (5) 60 mole-% of VC; (6) 40 mole-% of VC; (—) *trans*-DCE; (---) *cis*-DCE. Reaction temperature 50°C. Initiator AIBN, 0.1 mole-%.

transfer reaction to VC monomer is so stable with respect to the polymer radical that the free radical $\text{CH}_2=\text{CH}\cdot$ will contribute to termination rather than reinitiation. But, when carbon tetrabromide or dodecyl mercaptan is added, the rate of polymerization is increased, since the polymer radical will react with these chain transfer agents rather than VC monomer and, consequently, more reactive radicals will be produced.⁷ When *trans*-DCE was added to VC, the DP, the rate of polymerization, and the maximum conversion were lowered. It is considered from this result that the DCE radical $\text{CHCl}=\text{CH}\cdot$ is produced more easily than a VC radical because the chain transfer constant of DCE is larger than that of VC, but this radical seems to be more stable than the radical from VC.

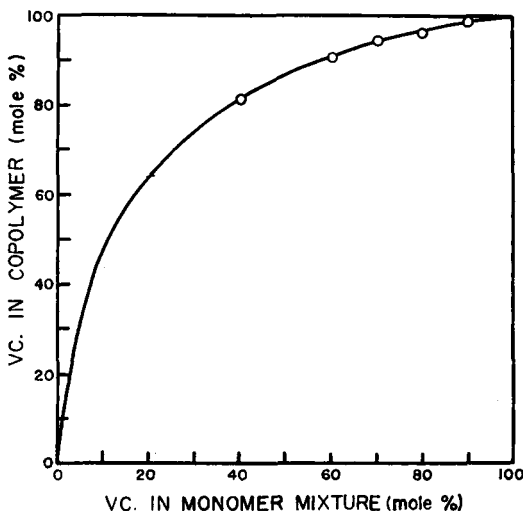


Fig. 2. Relationship between monomer and copolymer composition for copolymerization of VC with *trans*-DCE at 50°C.: (—) theoretical curve calculated from: r_1 (VC) = 5.39, r_2 (*trans*-DCE) = 0.072; (O) observed value.

Therefore, the frequency in the re-initiation reaction will be decreased, and the probability of degradation chain transfer will be increased, that is, the production of dimers by the combination of two DCE radicals or DCE radical with VC radical should be increased.

Thus, when the copolymerization was carried out at 50°C. at a DCE concentration of 40 mole-% in the monomer mixture, $[\eta]$ of the copolymer was about 0.05 ($[\eta]$ and DP of commercial PVC resin (Geon 103 EP) is 0.91 and 1050, respectively). This copolymer had no film-forming properties, but the T_g of this copolymer was 82°C., which was about 12°C. higher than that of the VC homopolymer polymerized under the same conditions.

The relationship between monomer and copolymer composition is shown in Figure 2, where the theoretical copolymerization curve is also shown on the basis of r_1 (VC) = 5.39, r_2 (*trans*-DCE) = 0.072; these values were

calculated from q , ϵ values estimated by Schwan and Price,⁸ the usual method^{8,9} being used.

As is shown in Figure 2, these theoretical values were essentially identical with observed values when the molar fraction of *trans*-DCE in the monomer mixture was maintained below 0.6.

Emulsion Polymerization at Low Temperature

As mentioned above, when the polymerization temperature was elevated, the DP was decreased markedly, owing to both effects of temperature and chain transfer reaction. So the emulsion copolymerization with redox initiator system was carried out at low temperature. Although, many redox initiator systems are given in the literature on the polymerization of VC, it was found in our preliminary experiment that the hydrogen peroxide-ferrous sulfate-ascorbic acid system was most useful initiator in the copolymerization of VC with DCE. Therefore, emulsion polymerization was carried out with this initiator system, and properties of polymers were investigated.

In the copolymerization, *trans*-DCE was used because it was found in the previous experiment that the *trans* isomer was more reactive than the *cis* isomer (see Fig. 1). The polymerization conditions and properties of copolymers and VC homopolymers polymerized at low temperature are given in Table I.

Reactivity of Monomers in Copolymerization

Monomer reactivity ratios in copolymerization of VC with DCE at -30°C . were calculated from q , ϵ values of each monomer as estimated by Schwan and Price⁸ by the same procedure used in the calculation of r_1 , r_2 at 50°C . The calculation gave values of 8.16 and 0.0291 for VC and *trans*-DCE, respectively at -30°C . The relationship between the conversion and the integral composition of the copolymer was calculated from monomer reactivity ratios of VC and *trans*-DCE at several compositions of the initial monomer mixture. These calculated values are shown in Figure 3 with solid lines. Observed values obtained from the monomer composition which contain 40 mole-% of *trans*-DCE are also shown in Figure 3 with open circles. Most of observed values lie below the theoretical curve (that is, the *trans*-DCE content in the copolymer is greater than that in the theoretical composition) and are in rather good agreement with the theoretical curve obtained from Q , e values at 50°C . (dotted line).

The kinetics of emulsion polymerization is more complicated than that of bulk polymerization because of the influence of such factors as the type and concentration of emulsifier, solubility of monomer in water, etc. Moreover, since methanol or a mixture of methanol and polyfunctional alcohol is added to the reaction mixture as an antifreezing agent, the change of solubility of monomer in the reaction mixture, that is the effect of distribution of monomers, should be considered. Owing to these effects, the observed reactivity of *trans*-DCE seems to be shifted.

TABLE I
Properties of VC-*trans*-DCE Copolymers and VC Homopolymers Polymerized at Low Temperature (-30°C).^a

Sample	Monomer molar ratio (VC/DCE) in charge	Conversion, %	DCE unit in copolymer, %	$[\eta]$, dl./g.	DP	T_g , $^{\circ}\text{C}$.	η_{sp} (at 180°C .), poise $\times 10^{-4}$	D_{633}/D_{632}	Solubility ^b		
									THF	CH	MEK
1	60/40	43.7	11.2	0.662	—	84-85	0.225	1.28	S	S	PS
2	60/40	39.5	12.3	0.781	—	92	0.360	1.15	S	S	PS
3	60/40	37.6	11.6	0.839	—	85-88	1.420	1.20	S	S	PS
4	60/40	34.9	12.1	0.866	—	86-88	3.05	1.17	S	S	PS
5	70/30	41.8	7.2	0.871	—	84	3.30	1.24	S	S	PS
6	80/20	59.8	5.5	0.880	—	78	6.08	1.22	PI	I	I
7 ^c	100/0	89.1	0	0.700	696	—	1.10	1.75	PS	PS	PI
8 ^d	100/0	69.9	0	0.830	903	—	22.7	1.67	I	I	I
9 ^e	100/0	88.0	0	1.380	2340	79	79.2	1.73	I	I	I
10	100/0	73.4	0	2.900	18880	78	63.2	1.77	I	I	I
PVC ^f				0.909	1050	76	0.210	1.28	S	PI	PS

^a Basic recipe: monomer, 100 g.; water, 120 g.; methanol, 80 g.; hydrogen peroxide (30% aq. soln.), 1.0 g.; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.02 g.; ascorbic acid, 0.6 g. emulsifier (sodium dodecylbenzenesulfonate), 1.6 g.

^b Solubility: S = soluble; PI = partially insoluble; PS = partially soluble; I = insoluble.

^c 100 g. CCl_4 added to the basic recipe.

^d 50 g. CCl_4 added to the basic recipe.

^e 25 g. CCl_4 added to the basic recipe.

^f Commercial PVC resin (Geon 103 EP).

As is shown in Figure 3, VC is so reactive compared to *trans*-DCE that the content of *trans*-DCE in the copolymer is less than that expected from the monomer composition at the initial stage of the polymerization. On the other hand, the content of *trans*-DCE in the monomer mixture is much

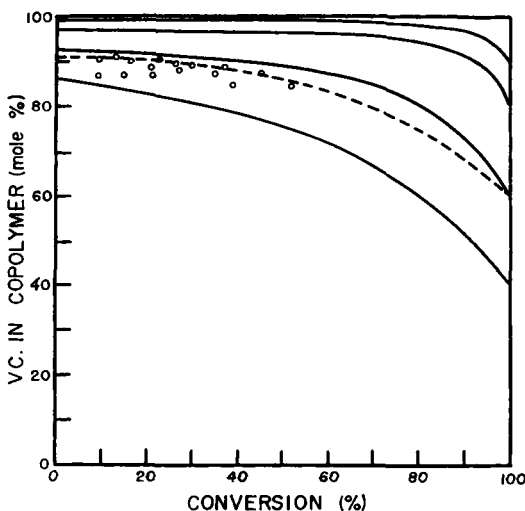


Fig. 3. Integral composition of copolymer vs. conversion in copolymerization of VC with *trans*-DCE at -30°C . at various initial monomer mixture compositions: (1) 10 mole-% DCE; (2) 20 mole-% DCE; (3) 40 mole-% DCE; (4) 60 mole-% DCE; (O) observed value (40 mole-% of DCE in the initial monomer mixture).

larger at the last stage of the polymerization than that at the initial stage; so the rate of polymerization is remarkably lowered. Therefore, the copolymerizations were not carried out beyond 50% conversion, in order to ensure the uniformity of the composition.

Glass Transition Temperature

Copolymer containing about 12% of *trans*-DCE had T_g of $84\text{--}92^{\circ}\text{C}$.; these values were $5\text{--}10^{\circ}\text{C}$. higher than that of the conventional PVC resin ($T_g = 76^{\circ}\text{C}$.) or VC homopolymers polymerized at low temperature under the same conditions ($T_g = 72\text{--}79^{\circ}\text{C}$.).

Although it was shown by Reding and his co-workers¹⁰ that the T_g of PVC increases with decreasing polymerization temperature (for example, T_g of PVC prepared at 40 , -10 , and -80°C . were 80 , 90 , and 100°C ., respectively), there was only a slight difference between the T_g of PVC polymerized in our laboratory at -30°C . and that of conventional PVC resin. The samples used for determination of T_g were compression-molded, and some samples, especially PVC polymerized at low temperature, strongly colored, but there was no change in the results of the elemental analysis and $[\eta]$ between the original sample and the colored ones.

Solubility

Solubilities of VC-*trans*-DCE copolymers, VC homopolymers polymerized at low temperature, and conventional PVC resin in several solvents were examined. The solubility of polymer is affected by the DP, but in the region of DP shown in Figure 2, almost of VC homopolymers polymerized at low temperature were not soluble in such solvents. On the other hand, most of the copolymers were soluble in tetrahydrofuran (THF) and cyclohexanone (CH) and partially soluble in nitrobenzene (NB) and methyl ethyl ketone (MEK) (Table I).

Melt Viscosity

As the η_m is much affected by the DP, η_m must be compared among the polymers which have the same DP. Considering the $[\eta]$, it is seen from the data in Table I that η_m of copolymers at 180°C. are lower than that of PVC polymerized at low temperature. These results are in good agreement with the fact that the molding of the PVC sheet polymerized at low temperature was very difficult. The color of the polymer (no stabilizer added) extruded from an orifice was dark brown for VC homopolymers and light brown for copolymers.

Weight Loss of the Polymer at Elevated Temperature

The plots of weight loss of the granulated polymers at 170°C. versus time are shown in Figure 4. The heat stability of the copolymers was much the

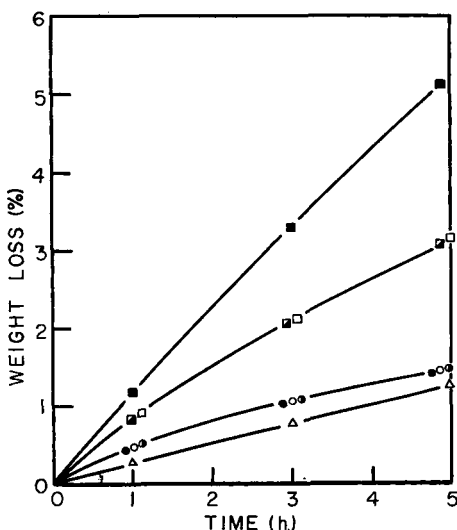


Fig. 4. Thermal decomposition of PVC and VC-*trans*-DCE copolymers at 170°C.: (Δ) conventional PVC resin (Geon 103EP); (\circ) sample 1; (\odot) sample 2; (\bullet) sample 3 (VC-*trans*-DCE copolymer); (\blacksquare) sample 8; (\square) sample 9, (\square) sample 10 (VC homopolymer). Sample numbers refer to Table I.

same as that of the conventional PVC resin, but VC homopolymers polymerized at low temperature were less stable than the others and quickly turned dark brown in color.

Infrared Absorption Spectra

The stereoregularity of the polymers was measured by the ratio D_{635}/D_{692} of the 635 and 692 cm.^{-1} infrared absorption bands.¹¹ The results of the measurements are given in Table I. It has been shown by Rosen and Marshall¹² in the copolymerization of VC with vinyl acetate that the D_{635}/D_{692} ratio decreased with increasing vinyl acetate content in the copolymer. Similarly in the result of copolymerization of VC with *trans*-DCE, it was found that the D_{635}/D_{692} ratio decreased apparently on incorporation of about 5% of *trans*-DCE with the VC.

In case of the copolymers of VC with *trans*-DCE, the absorption band, presumed by Fukawa et al.² to be the absorption caused by two adjacent C—Cl bonds situated at the *trans* position, was recognized at 750 cm.^{-1} , unlike the copolymer of VC with *cis*-DCE.

DISCUSSION

The intrinsic viscosities of the copolymers prepared at high temperature were very low. Therefore, these copolymers had not film-forming ability, but the T_g values were higher than those of conventional PVC resin and VC homopolymer prepared at low temperature. Since both copolymers polymerized at high and low temperatures have high T_g , it seems reasonable to assume that the increase in the T_g is not attributable the decrease in polymerization temperature but is rather caused by incorporating *trans*-DCE into the copolymer.

Fordham¹³ indicated in his theoretical study of polymerization of VC that the potential energy difference between syndiotactic and isotactic configuration is calculated to be of the order of 1.5–2.0 kcal./mole, in favor of the former, and that the syndiotactic configuration and crystallinity increase as the polymerization temperature is decreased. Moreover, increases in T_g and melting point caused by the increase in crystallinity have been also recognized.¹⁰ However, it was found that, in cases of the copolymers of VC with *trans*-DCE, the T_g were increased on incorporation of *trans*-DCE unit into the copolymer in spite of a decrease in the D_{635}/D_{692} ratio (that is, decrease in the stereoregularity).

It has been found in the copolymerization of VC with diethyl maleate that minimum number-average sequence length \bar{n} of VC which gives the crystallinity to the copolymer is 20–30.¹⁴ On the other hand, the estimated value of average sequence length of VC in the copolymer containing about 12% of *trans*-DCE (for example, Nos. 1–4 in Table I) was 9 on the basis of eq. (2).

$$\bar{n} = ([M_2] + r_1[M_1])/[M_2] \quad (2)$$

In this equation,¹⁵ $[M_1]$, $[M_2]$ refer to the molar fraction of VC and *trans*-DCE, respectively, in the monomer mixture, and r_1 is the monomer reactivity ratio of VC.

Consequently, it is likely that the degree of crystallinity of these copolymers is lowered remarkably.

From the standpoint of the increase in solubility, it is also presumed that the copolymer of VC with *trans*-DCE has a lower degree of crystallinity than VC homopolymers prepared at low temperature and conventional PVC resin. Thus, it seems unlikely that, in cases of these copolymers, the increase in the crystallinity can be a major factor contributing to the increase in the T_g .

Generally, following two factors can be considered as the cause of the increase in the T_g by the introduction of a foreign monomer unit: (1) the increase in the interaction between polymer chains resulting from the introduction of a polar substituent; (2) the prevention of the free rotation of the polymer chain by the introduction of a bulky substituent. In the copolymer of VC with *trans*-DCE polymerized at low temperature, the solubility was much higher than that of VC homopolymer polymerized under the same condition, and it is also known that the solubility increases when a proper quantity of 1,1-dichloroethylene unit (vinylidene chloride unit) is incorporated into PVC, despite the increase in the chlorine content of the copolymer.¹⁶

As the interaction between polymer chains increases, the solubility of the polymer should decrease, but, as is shown in Table I, the solubility of the copolymer is rather increased by the introduction of the *trans*-DCE unit. Therefore it is presumed from this solubility behavior of the copolymer that the introduction of *trans*-DCE unit into the VC polymer contributes to the disruption of the copolymer crystal (which brings about a decrease in the interaction between polymer chains and an increase in the solubility) rather than to the increase in the interaction between polymer chains.

From this point of view, the increase in the stiffness of the polymer chain caused by the introduction of bulky DCE unit must be considered as the major factor in the increase in the T_g of this copolymer rather than the effect of an increase in the interaction between polymer chains through the polar chlorine atoms or by an increase in crystallinity.

Since it is considered that the dispersion of the copolymer chains in the solvent is not disturbed substantially even if the stiffness of the molecule is increased by the increase in the chlorine content, both increase in the T_g and the solubility obtained in this experiment can be well explained from these facts.

It is known that an increase in the vinylidene chloride content in the copolymer of VC with vinylidene chloride in the VC-rich region brings about a decrease in both the solubility and softening point.¹⁶ Therefore, it seems that the 1,1-dichloroethylene unit in the VC copolymer is not effective to the increase in the stiffness of the polymer chain and only the existence of 1,2-dichloroethylene unit bring about the increase in both T_g and the solubility.

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Résumé

La copolymérisation du chlorure de vinyle avec le *trans*-1,2-dichloroéthylène a été effectuée à différentes températures, et les propriétés des copolymères, obtenus par la copolymérisation en émulsion à basse température, ont été examinées. Dans le cas de la copolymérisation en bloc à températures plus élevées que la température de chambre, la vitesse de polymérisation, la conversion à l'équilibre, et la $[\eta]$ sont abaissées par augmentation de la teneur en *trans*-1,2-dichloroéthylène dans le mélange initial des monomères, mais la T_g et le point de ramolissement des copolymères contenant environ 15% d'unités 1,2-dichloroéthylène étaient d'environ 10°C plus élevés que pour la résine de PVC conventionnelle, malgré leur inaptitude à former des films. Les rapports de réactivité des monomères à 50°C étaient de 5.39 (VC) et 0.072 (*trans*-DCE) respectivement. La copolymérisation en émulsion a été effectuée à -30°C, en employant un système initiateur redox (peroxyde d'hydrogène-sulfate ferreux-acide ascorbique), afin d'augmenter dans les deux cas la $[\eta]$ et la vitesse de polymérisation. Les copolymères à basse température avaient une T_g plus élevée et une meilleure solubilité que le VC-homopolymère, polymérisé dans les mêmes conditions ou que la résine de PVC conventionnelle. A partir des résultats des spectres d'absorption infra-rouge, des solubilités et du calcul de la longueur de séquence des unités de VC-monomère dans la chaîne polymérique, on suppose que la stéréorégularité et la cristallinité des copolymères à basse température sont plus basses que celles des VC-homopolymères à basse température. On en a conclu qu'une T_g plus élevée et une bonne solubilité du copolymère à basse température étaient dues à l'empêchement de la rotation libre dans la chaîne polymérique provoquée par la distribution statistique du composant 1,2-dichloroéthylène dans la chaîne polymérique.

Zusammenfassung

Die Kopolymerisation von Vinylchlorid mit *trans*-1,2-Dichloräthylen wurde bei verschiedenen Temperaturen durchgeführt und die Eigenschaften der durch Emulsionskopolymerisation bei niedriger Temperatur erhaltenen Kopolymeren untersucht. Im Falle der Kopolymerisation in Substanz bei höheren Temperaturen als Raumtemperatur

wurde die Polymerisationsgeschwindigkeit, der Gleichgewichtsumsatz und $[\eta]$ mit zunehmendem Gehalt an *trans*-1,2-Dichloräthylen der Ausgangsmonomermischung herabgesetzt; T_g und der Erweichungspunkt der Kopolymeren mit etwa 15% 1,2-Dichloräthylen lagen jedoch um etwa 10°C höher als bei konventionellem PVC-Harz, obgleich die Kopolymeren zur Filmbildung unfähig waren. Das Monomerreaktivitätsverhältnis bei 50°C betrug 5,39 (VC) und 0,072 (*trans*-DCE). Die Emulsionskopolymerisation bei -30°C wurde mit einem Redoxstartersystem (Wasserstoffperoxyd-Ferrosulfat-Ascorbinsäure) ausgeführt, um sowohl $[\eta]$ als auch die Polymerisationsgeschwindigkeit zu erhöhen. Die Tieftemperaturkopolymeren besaßen ein höheres T_g und eine bessere Löslichkeit als unter gleichen Bedingungen erhaltenes VC-Homopolymeres oder konventionelles PVC-Harz. Aus den Infrarotabsorptionsspektrographischen Ergebnissen, aus der Löslichkeit sowie aus der Berechnung der Sequenzlänge von VC-Monomereinheiten in der Polymerkette wurde geschlossen, dass die Stereoregularität und die Kristallinität der Tieftemperaturkopolymeren geringer waren als diejenigen der Tieftemperatur-VC-Homopolymeren. Weiters wurde geschlossen, dass der höhere T_g -Wert und die gute Löslichkeit des Tieftemperaturkopolymeren durch die Verhinderung der freien Rotation der Polymerkette durch statistische Verteilung der 1,2-Dichloräthylenkomponente in der Polymerkette zustande kommt.

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