Polymer Bulletin 1, 253-258 (1979)

Polymer Bulletin

Preparation of Poly(Vinyl Chloride-g-Isobutylene) by BCl_3

S. N. Gupta and J. P. Kennedy

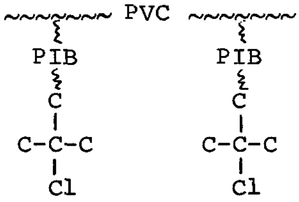
Institute of Polymer Science, University of Akron, Akron, Ohio 44325, USA

Summary

Poly(vinyl chloride-g-isobutylene) has been synthesized using mildly dehydrochlorinated (NaOH treated) PVC in conjunction with BCl_3 coinitiator. Treatment of PVC with NaOH increases initial thermal dehydrochlorination rate and renders the polymer suitable for efficient grafting. Untreated PVC produces negligible grafting.

Introduction

The discovery that BCl_3-coinitiated isobutylene polymerizations terminate by chlorination and lead to terminal tertiary chlorines (KENNEDY et al. 1977a) opened numerous new polymer synthetic possibilities including novel block copolymer preparations (KENNEDY et al. 1978). This discovery coupled with our understanding of initiation details of BCl_3-coinitiated polymerizations, i.e., initiation is due to carbenium ions generated by BCl_3 from suitable precursors (KENNEDY et al. 1977a), led us to postulate graft copolymerization initiation by suitable macrocation precursors in the presence of BCl_3 coinitiator. On the basis of these facts (KENNEDY et al. 1977a) (KENNEDY et al. 1978) we set out to initiate isobutylene polymerizations by poly(vinyl chloride) (PVC) cations in conjunction with BCl_3 and thus to prepare poly(vinyl chloride-g-isobutylene) containing terminal tertiary chlorines at the branches:



0170-0839/79/0001/0253/$01.20

Scouting experiments carried out by utilizing extensive past experience in PVC graft copolymer synthesis (KENNEDY, DAVIDSON 1977) showed that although our basic premises were sound, the extent of grafting (PIB add-on) from virgin PVC backbones was negligible. Analysis of these results led us to conclude that low grafting was mainly due to (1) the presence of very low amounts of labile (allylic) chlorines in PVC (0.1 to 0.2 mole %) (ROBILA et al. 1977) and (2) that initiation by allylic chlorines in conjunction with BCl_3 is not very efficient. Low initiation efficiency of allylic chlorine-BCl_3 combinations has been established by model experiments (KENNEDY et al. 1977b). To overcome these difficulties we theorized that increased amounts of allylic chlorines in the chain may be obtained by using partially degraded PVC. Thus to increase allylic chlorine concentration in the backbone we studied PVC dehydrochlorination under controlled conditions and have used mildly degraded PVCs for grafting isobutylene. Preliminary results in this communication indicate that reasonable grafting of isobutylene from mildly degraded PVC can be achieved.

PVC Dehydrochlorination

According to previous workers (ROTH et al. 1960) (BENGOUGH, VARMA 1966) base-induced dehydrochlorination of PVC occurs readily at room temperature and preferentially produces short polyene sequences. Due to the random nature of this chemical reaction, the polyenes are expected to be randomly distributed along the PVC chain. Extent of dehydrochlorination and polyene lengths may be controlled by base concentration, PVC to base ratio, solvent and temperature.

Experimental And Results

Keeping in mind our objectives (mild degradation with shortest possible polyene sequences to prevent resin discoloration) and our experience of previous studies, we developed the following procedure to increase allylic chlorine concentration in PVC.

PVC samples (K38, Borsod Chemical Works, Hungary) were dissolved in 1,2 dichloroethane to make 1% solution. While stirring under a N_2 atmosphere 5% by volume of methanol was added to the PVC solution followed by the addition of 5% by volume of 1% NaOH solution in methanol. The reaction was allowed to continue for a desired period of time. The polymer was precipitated in excess methanol, redissolved in THF, centrifuged and reprecipitated in excess methanol, filtered and dried under vacuum. The polymer was either colorless or faintly yellowish depending on the extent of dehydrochlorination i.e., time of NaOH treatment. Thermal dehydrochlorination rates of PVC before and after NaOH treatment are shown in Figure 1 and Table 1.

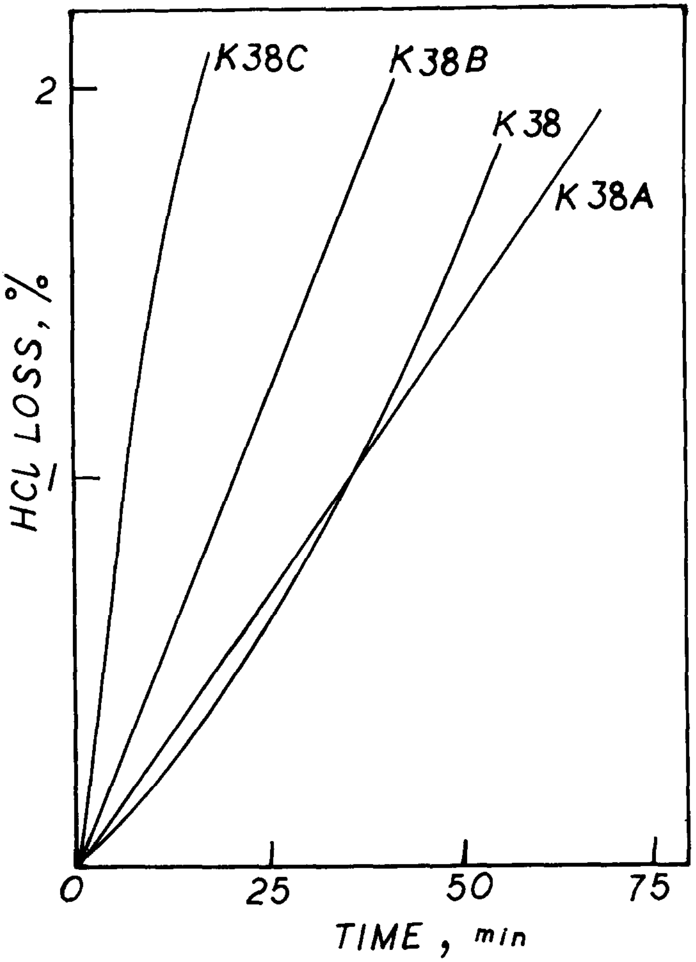


Fig. 1. Dehydrochlorination rates of PVC before and after treatment with NaOH. Dehydrochlorination at 190°C under N_2.

TABLE 1

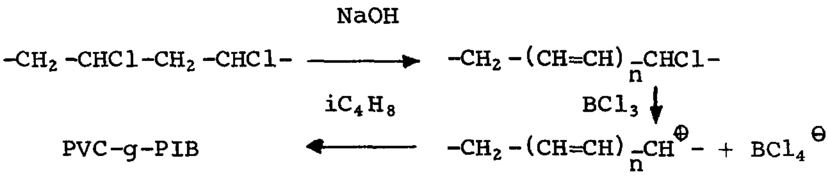
Synthesis of Poly(vinyl chloride-g-isobutylene)

Sample No.	NaOH treatment of PVC		Initial dehydrochlorination rate at 190°C	PIB Content in graft	GE	iC_4H_8 conversion
	NaOH/PVC mole ratio	Time Min.	$min^{-1} \times 10^5$	%	%	%
K38	0	0	22.5	0.5	0	16
K38A	0.11	10	29.0	3.2	17	18
K38B	0.08	60	50.0	11.0	41	28*
K38C	0.11	60	166.7	22.5	70	33

*Polymerization temperature, -50°C

Grafting experiments were carried out in a dry box under a N_2 atmosphere using culture tubes and methylene chloride solvent at -75°C. A 2% solution of PVC samples, 0.9M isobutylene and 10^{-2}M BCl_3 were used. Graftings were continued for an hour with occasional shaking, the reactions were terminated by a little methanol and the polymer precipitated in methanol. Polyisobutylene (PIB) was separated with n-pentane. The amount of grafted PIB in the n-pentane insoluble part was determined by infrared spectroscopy. Grafting efficiency (GE) = (Wt. of PIB grafted to PVC X 100) /(Total wt. of PIB produced). Results are shown in Table 1.

The reaction scheme can be given as follows:



$$\begin{tikzcd}
\mathrm{-CH_2-CHCl-CH_2-CHCl-} \arrow[r, "\mathrm{NaOH}"] & \mathrm{-CH_2-(CH{=}CH)_n-CHCl-} \arrow[d, "\mathrm{BCl_3}"'] \\
\mathrm{PVC\text{-}g\text{-}PIB} & \mathrm{-CH_2-(CH{=}CH)_n-CH^{\oplus}-} + \mathrm{BCl_4^{\ominus}} \arrow[l, "\mathrm{iC_4H_8}"']
\end{tikzcd}$$

We consider it possible that chain transfer to allylic chlorines on the polymer also occurs and yields PIB.

According to the results the extent of grafting and isobutylene conversion increase with increasing initial thermal dehydrochlorination rate. This can be explained by assuming that the initial dehydrochlorination rate is proportional to the labile allylic chlorine content of the polymer.

References

1. W. I. BENGOUGH and I. K. VARMA : Eur. Polym. J. 2, 61 (1966)
2. J. P. KENNEDY, S. Y. HUANG and S. C. FEINBERG: J. Polym. Sci., Polym. Chem. Ed. 15, 2801 (1977a)
3. J. P. KENNEDY and D. L. DAVIDSON : J. Appl. Polym. Sci., Symp. Issue 30, (1977)
4. J. P. KENNEDY, S. Y. HUANG and S. C. FEINBERG: J. Polym. Sci., Polym. Chem. Ed. 15, 2869 (1977b)
5. J. P. KENNEDY, S. C. FEINBERG and S. Y. HUANG: J. Polym. Sci., Polym. Chem. Ed. 16, 243 (1978)

6. G. ROBILA, E. C. BURUIANA and A. A. CARACULACU: Eur. Polym. J. 13, 21 (1977)
7. J. P. ROTH, P. REMPP and J. PARROD: Compt. Rend. 251, 2356 (1960)

Received November 6, 1978