Polymer Bulletin 1, 79–84 (1978)

Polymer Bulletin

Reversible Crosslinking During Thermal Degradation of PVC

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Introduction

Thermal degradation of PVC has been the subject of many investigations (BRAUN 1971, AYREY et al 1974). The primary process of thermal degradation is the zipping off of hydrogen chloride and formation of polyene sequences containing different numbers of conjugated double bonds in the chain. The polyenes are highly reactive and may participate in secondary reactions (TÜDŐS et al. 1974, KELEN 1978). During thermal degradation of solid PVC samples crosslinking and gel formation is observed. The kinetics and characteristics of this process have been investigated by several workers (BENGOUGH and SHARPE 1963, KURZWEIL and KRATOCHVIL 1969, NAGY et al. 1976, IVÁN et al. 1978). Two mechanisms were suggested for crosslinking. According to some authors crosslinking takes place during the primary process (DRUESEDOW and GIBBS 1953, FUCHSMANN 1959, WINKLER 1959, BENGOUGH and SHARPE 1963, MARKS et al. 1967, KURZWEIL and KRATOCHVIL 1969, ABBÅS and SŐRVIK 1973), e.g., by interchain elimination of HCl, whereas others suggest intermolecular Diels-Alder reaction between the conjugated polyene sequences (RAZUVAEV et al. 1966, TROITSKII and MYAKOV 1967, ZILBERMAN et al. 1974). There is little hard evidence in the literature in favor of either of these mechanisms. In this paper evidence is presented that intermolecular Diels-Alder reactions of polyenes are at least partly responsible for crosslinking during PVC degradation.

Experimental

Experiments were carried out with samples having different K-values (FIKENTSCHER K). Powdery PVC samples were heated under a constant stream of argon (5 l/h) at 180°C. Gel content (γ, weight fraction)

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0170-0839/78/0001/0079/$01.20

was determined gravimetrically.

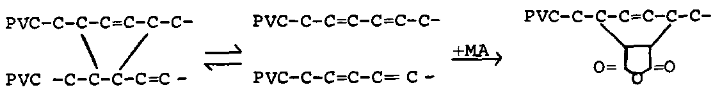
Degraded PVC samples were treated with excess maleic anhydride (MA) in cyclohexanone solution under argon atmosphere at 80-85°C for three hours. After treatment with MA, GPC measurements or gel content determinations were carried out.

GPC measurements were carried out using five Styragel columns (10^6, 10^5, 10^4, 10^3, 500 Å) and a Waters R401 Differential Refractometer at 25°C and 0.8 ml/min tetrahydrofuran. Two ml samples of 2 mg/ml were injected. The column set was calibrated with PS standards (Waters) and PVC standards (National Physical Laboratory). Chromatograms were corrected for broadening (PIERCE and ARMONAS 19682 and universal calibration (GRUBISIC et al. 1967) was used to calculate MWD and molecular weight averages.

Results and Discussion

Very early during thermal degradation of PVC crosslinking occurs and the polymer becomes partially insoluble after a well-defined degradation time (gel point). Crosslinking can be followed either by MWD or molecular weight average determinations prior to the gel point, or by gel content determination after the gel point. Both methods have been used in this study.

It was postulated that one could distinguish between the two possible crosslinking mechanisms i.e., interchain HCl elimination or intermolecular Diels-Alder reaction, by adding MA to swollen heat degraded PVC gels. If crosslinking during thermal degradation occurs by Diels-Alder reaction, the addition of an excess of a strong dienophile, e.g., MA, to heated PVC gels should eliminate crosslinks and bring the sample in solution. MA will preferentially react with the dienes in the degraded PVC chain and thus displace the Diels-Alder/retro-Diels-Alder equilibrium:



Experimentally, when thermal degradation of PVC was carried out for periods shorter than necessary for gel formation, treatment with maleic anhydride resulted in a decrease in molecular weight averages. The values were between those of the undegraded and degraded polymer (Table I).

TABLE I

Molecular Weight Averages of Heat Degraded PVC. (K=49, $\overline{M}_w$ of undegraded PVC 4.90x10^4)

Degradation time (min)	Degraded samples	Degraded and subsequently maleic anhydride treated samples
	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_w \cdot 10^{-4}$
60	5.48	5.13
120	7.06	5.91
180	9.54	6.26

Due to crosslinking, the MWD of degraded PVC shows significant broadening in the higher molecular weight region. After MA treatment this broadening partially disappears and the MWD of the degraded PVC approaches that of the undegraded sample. (Fig. 1)

Advanced thermal degradation of PVC produces not only occasional crosslinks but insoluble gel. The onset of gel formation (gel point) is well defined. Samples degraded beyond the gel point but to only relatively low gel contents (up to 15% insoluble) became entirely soluble upon treatment with MA. Samples with higher gel contents remained partly insoluble even after treatment with MA, however their gel content decreased drastically. (Fig. 2)

These results indicate that a large portion of the crosslinks formed during thermal degradation of PVC are reversible. Only Diels-Alder crosslinking of conjugated polyene sequences during heat degradation of PVC can explain (partial) crosslinking reversibility observed. The presence of other crosslinking mechanisms, e.g., recombination of polyenyl radicals, cannot be excluded because crosslinking has not been completely eliminated. However, even if all the crosslinks were formed via Diels-Alder reaction full reversibility would not be expected because the polyenes involved in crosslinks may undergo irreversible reactions as well.

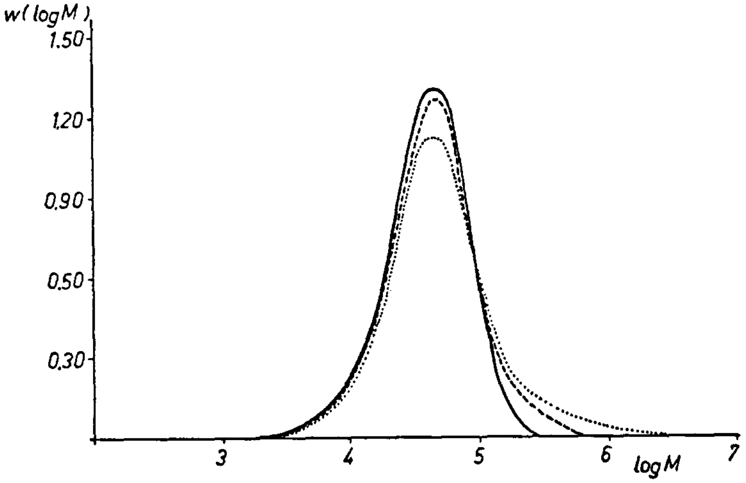


Fig. 1 Molecular Weight Distribution of Undegraded K=49 Samples (—), degraded for 180 min (...) and treated with maleic anhydride after degradation (---).

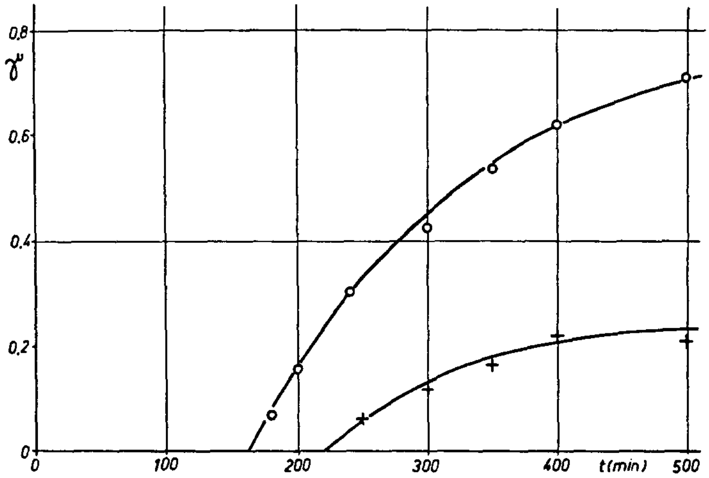


Fig. 2 The Effect of Degradation Time on Insoluble Fraction (PVC K = 79.5). O = without MA treatment, + with MA treatment.

As shown by the data in Fig. 2, at least 60-70% of the originally insoluble polymer became soluble upon treatment with MA.

Summary

PVC undergoes rapid crosslinking during thermal degradation. Diels-Alder addition of conjugated polyenes was proposed as a possible crosslinking mechanism by earlier authors. By the use of conditions favoring retro Diels-Alder reaction of crosslinks (treatment with maleic anhydride at elevated temperature) it was proved that crosslinks are largely reversible. Evidently Diels-Alder addition of the conjugated polyenes plays an important role in crosslinking during thermal degradation of PVC.

Acknowledgement

The authors gratefully acknowledge financial contributions by the Institute for Cultural Relations, Hungary and the National Science Foundation, USA.

References

K.B. ABBÅS and E.M. SÖRVIK: J. Appl. Polym. Sci., 17, 3577 (1973)

G. AYREY, B.C. HEAD and R.C. POLLER: J. Polymer Sci., Macromol. Rev., 8, 1 (1974)

W.I. BENGOUGH and H.M. SHARPE: Makromol. Chem., 66, 31, 45 (1963)

D. BRAUN: Gummi Asbest Kunstst., 24, 1116 (1971)

D. DRUESEDOW, C. G. GIBBS: Nat. Bur. Stand. Circular No. 525, 69 (1953)

C.H. FUCHSMANN: SPE Techn. Papers, 5, 1 (1959)

Z. GRUBISIC, P. REMP and H. BENOIT: J. Polym. Sci., B5, 753 (1967)

B. IVÁN, B. TURCSÁNYI, T.T. NAGY, T. KELEN and F. TÜDŐS: Polymer, 19, 351 (1978)

T. KELEN: J. Macromol. Sci.-Chem. (in press)

K. KURZWEIL and P. KRATOCHVIL: Collect. Chem. Commun., 34, 1429 (1969)

G.L. MARKS, J.L. BENTON and C.M. THOMAS: SCI Monographs, 26, 204 (1967)

T.T. NAGY, T. KELEN, B. TURCSÁNYI and F. TÜDŐS: Reaction Kinetics and Cat. Letters, 5, 309 (1976)

P.E. PIERCE and J.E. ARMONAS: J. Polym. Sci., Part C, 21, 23 (1968)

G.A. RAZUVAEV, L.S. TROITSKAWA, V.N. MYAKOV and B.B. TROITSKII: Dokl. Akad. Nauk. SSSR. Khim., 170, 1342 (1966)

B.B. TROITSKII and V.N. MYAKOV: Plast. Massy, 135 (1967)

F. TÜDŐS, T. KELEN, T.T. NAGY and B. TURCSÁNYI: Pure Appl. Chem., 38, 201 (1974)

D.E. WINKLER: J. Polym. Sci., 35, 3 (1959)

E.N. ZILBERMAN, E.M. PEREPLETCHIKOVA, E.N. GETMANENKO and E.G. POMERANCEVA: Vysokomol. Soed., B16, 46 (1974)

Received July 31, 1978