Polymer Bulletin 3, 613-620 (1980)

Polymer Bulletin

Crosslinking, Scission and Benzene Formation During PVC Degradation Under Various Conditions

Tibor T. Nagy, Béla Iván, Béla Turcsányi, Tibor Kelen and Ferenc Tüdős

Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
POB 17, 1525 Budapest, Hungary

Summary

The kinetics and mechanism of crosslinking and chain scission has been studied on several PVC samples during thermal, thermooxidative, dynamic, and HCl catalyzed degradation. During pure thermal degradation crosslinking at a constant rate without scission occurs, while in the presence of oxygen and/or shear scission is not negligible. In the dynamic test, under shear both processes are fast, compared to static tests. The mechanism of benzene formation without main chain scission is discussed.

Introduction

At elevated temperature PVC degrades with the formation of HCl and polyenes. It has been known that in inert atmosphere crosslinking dominates, while oxygen leads to chain scission (e.g. ARLMAN, 1954). Despite of the large number of papers on PVC degradation only few deal with the kinetics and mechanism of these processes. Crosslinking of concentrated PVC solutions was shown (BENGOUGH and SHARPE 1963) to follow second order kinetics. ABBÅS and SÖRVIK (1973) found only crosslinking in N_2, and scissions in pure O_2 at the early stages of the degradation, while KURZWEIL and KRATOCHVIL (1969) reported simultaneous scissions and crosslinking both in N_2 and air. Several authors claim that network formation occurs in the primary process of pure thermal degradation (e.g. BENGOUGH and SHARPE 1963, ABBÅS and SÖRVIK 1973, SVÉTLY et al. 1980) but others regard it as a secondary reaction of earlier formed polyenes, i.e., Diels-Alder cycloaddition between polyene sequences (RASUVAEV et al. 1966, ZILBERMAN et al. 1974). The kinetics and some aspects of mechanism of network formation and main chain scission during PVC degradation has been investigated by our group in the last years (NAGY et al. 1976, IVÁN et al. 1978, 1980, KELEN et al. 1978). This paper concerns comparison of network formation kinetics of several suspension polymerized samples in thermal degradation and discusses influences of HCl, oxygen, shear and temperature on this process. The mechanism of benzene formation obtained during pure thermal decomposition is also discussed.

Experimental

Some of the PVC samples used in this study were laboratory products, others commercial suspension polymers, covering a broad range of average molecular mass. They received no other treatment than washing and drying after the polymerization.

Degradation was carried out on powder samples in glass vessels under Ar or O_2 stream as described earlier (KELEN et al. 1978, IVÁN et al. 1980). At predetermined degradation time the heat treatment was interrupted and gel content was gravimetrically measured, or - prior to the gel point - molecular mass distribution was determined by GPC. Dynamic degradation tests were conducted in the mixing chamber of HAAKE RHEOCORD at 20 rpm and 180°C set temperature, 60 g load. Further experimental details are under publication (PUKÁNSZKY et al.in print). Mixing was interrupted for a few seconds, small samples were taken from the chamber and gel content was determined.

Gel point was determined also by the earlier proposed photometric method (IVÁN et al. 1978), by taking UV and visible spectra, and plotting the optical density of the sol phase against time.

Results and discussion

The number average polymerization degree, polydispersity and gel point data measured during thermal degradation at 175°C in inert atmosphere are collected in Table 1.

TABLE 1

Number average polymerization degree (P_n), polydispersity (P_w/P_n), gel point (t_g), HCl loss conversion at gel point (ξ_g) and number of eliminated HCl molecules per formed crosslinks ($2\xi_g/q$). Degradation: powder at 175°C in Ar stream.

Sample	P_n	P_w/P_n	t_g (min)	$\xi_g \cdot 10^2$	$2\xi_g/q$
1	232	1.99	348	3.27	30
2	344	2.39	365	2.83	39
3	643	1.83	295	1.81	47
4	670	2.12	234	2.15	58
5	731	1.92	190	0.98	29
6	749	2.05	230	0.88	26
7	797	1.67	355	2.16	68
8	841	1.80	280	1.89	64
9	859	1.84	375	1.32	45
10	874	2.00	455	1.73	60
11	888	1.73	245	1.72	61
12	1073	1.78	345	1.69	72
13	1117	2.16	270	1.40	63

The polydispersities (P_w/P_n) of all samples are closely 2, so one can assume, that their molecular weight distribution can be approximated by the "most-probable" (Flory) distribution, which simplifies the evaluation of data. For polymers of this distribution in case of constant crosslinking and scission rate the following equation can be applied (CHARLESBY and PINNER 1959):

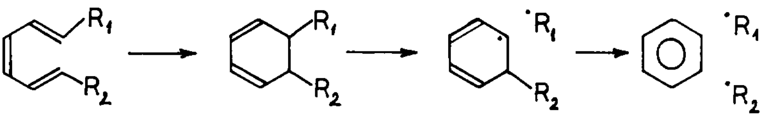
$$s + \sqrt{s} = \frac{v_p}{v_q} + \frac{1}{v_q P_n} \cdot \frac{1}{t} \qquad (1)$$

where s is the soluble fraction, v_p and v_q are the rates of scission and crosslinking resp. and P_n is the number average polymerization degree of the original polymer, t denotes time.

In pure thermal degradation essentially linear CHARLESBY-PINNER plots were obtained with zero intercept, indicating that scission is negligible in this case. Typical examples are shown on Fig.1.

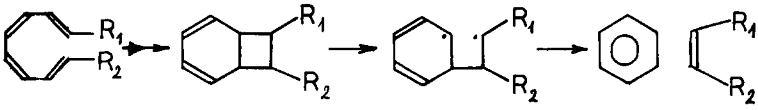
The absence of chain scissions is very interesting in regard of the benzene formation mechanism. As it was shown recently by isotopic labelling, benzene formation is exclusively intramolecular (O'MARA 1977, LATTIMER and KROENKE 1980). The precursors of the benzene molecules are obviously the cyclic structures formed on the polyene sequences in secondary processes (TÜDŐS et al.1974). The time lag of the benzene formation curve is in accord with this reaction sequence (Fig.2).

For the benzene formation without net chain scission three possibilities are open: (i) the benzene is formed on the chain end, (ii) the benzene is formed by chain scission, but the free chain ends recombine again and (iii) free chain ends are formed not at all in this process. As the polyene sequences are formed statistically on the polymer chain, the first possibility is expected to be insignificant. For the remaining two cases the following mechanisms are considered (STARNES and EDELSON 1979, STARNES in print):



(2)

and



(3)

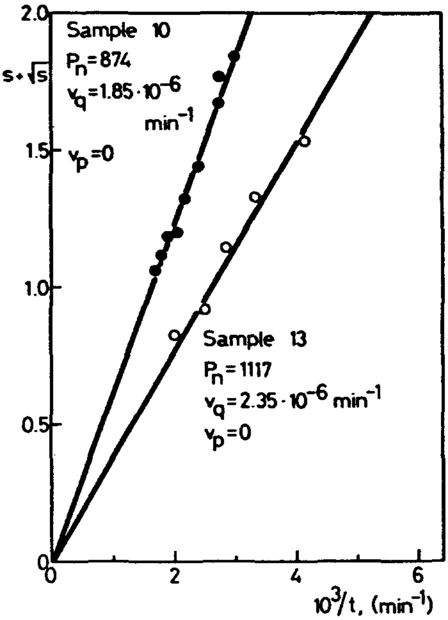


Figure 1.
CHARLESBY-PINNER plots of thermally degraded PVC powders. (180°C, Ar)
●: sample 10,
o: sample 13

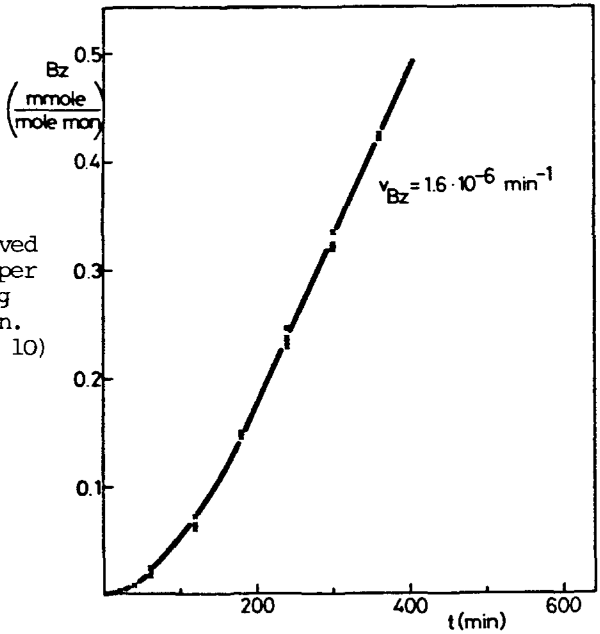


Figure 2.
The number of evolved benzene molecules per monomer unit during thermal degradation. (180°C, Ar, sample 10)

Scheme (2) must be obviously completed by the further reactions of the radicals R_1 and R_2. If these recombine quantitatively, no net chain scission results, in case of some disproportionation, however, the benzene formation is accompanied by chain scissions. The slight decrease of intrinsic viscosity of PVC degraded in solution, observed by us (NAGY 1976, KELEN 1978) motivate the authors to favour Scheme (2). We must emphasize here, however, that this decrease is so small (about 6% in 300 min at 200°C for 1% solution of sample 10 of this paper) that it rather affirms the negligibility of the scission process related to the benzene formation. Clearly, the present experimental informations are not sufficient to prove either of the above two mechanisms. We prefer Scheme (3) on two grounds: First, if the R_1, R_2 groups are unsaturated - which occur with high probability as the cyclic structures are more readyly formed from long polyenes (TÜDŐS et al. 1974) - the structure of the radicals formed by sequence (2) must be the highly improbable vinylic type (~CH=CH·). On the other hand, on low molecular mass tetraenes cyclization (HUISGEN et al. 1967) and recently even benzene formation under relatively mild conditions (MARVELL et al. 1978) was reported. A Scheme practically identical with (3) was proposed by us (NAGY et al. 1973, 1980) independently of STARNES and EDELSON.

The rate of crosslinking increases paralell with the overall rate of degradation when the temperature is increased. The data collected in Table 2 show, that in the case of pure thermal degradation the ratio of eliminated HCl to formed crosslinks ($2\xi/q$) does not vary much with temperature, i.e., the overall activation energy of crosslinking and of thermal dehydrochlorination are about the same: nearly 125 kJ/mole (~30kcal/mole).

The number of HCl molecules per crosslinks ($2\xi_g/q$) varies between 26 and 72 on the investigated 13 samples and gives about 50 on the average. Similar value was reported recently (SVĚTLY et al. 1980), but the 5 samples investigated by them showed little variation of the ξ_g/q ratio.

TABLE 2

Temperature dependence of gel point (t_g), conversion at the gel point (ξ_g) and ratio of eliminated HCl to formed crosslinks ($2\xi_g/q$) of sample 4 during degradation in inert atmosphere.

Temp. °C	t_g min	$\xi_g \cdot 10^2$	$2\xi_g/q$
170	312	1,94	52
175	234	2,15	58
180	152	2,05	55
190	70	1,90	51
200	38	2,00	54

The kinetics of network formation changes significantly with degradation conditions. If degradation is carried out in a closed system under the evolved HCl the gel point is reached earlier, but the ratio of eliminated HCl to crosslinks increases, indicating that the catalytic effect of HCl on elimination is more pronounced than on crosslinking. For example, $t_g = 180$ min and $\xi_g = 2.5$ % in a closed evacuated system, while $t_g = 310$ min and $\xi_g = 1.6$ % during pure thermal degradation under Ar stream for sample 10 at 180°C.

One may assume, that in presence of HCl the mechanism of PVC degradation remains essentially the same, as in absence (precisely, at very low levels) of HCl. In oxygen atmosphere, however, further processes become operative and the chain scission rate is comparable with that of the crosslinking rate. Interestingly, the Charlesby-Pinner plots also show good linearity in case of thermooxidative degradation, consistent with constant and independent scission and crosslinking rates (Fig.4). More detailed discussion of this phenomenon has recently been reported in this journal (IVÁN et al. 1980).

Under dynamic conditions in the mixing chamber PVC is exposed besides heat, HCl and oxygen also to mechanical shear. The change of torque (M), material temperature (T) and gel fraction (1-s) during the dynamic degradation test for sample 10 are given on Fig.3. The following phases can be distinguished on the torque curve: when the material is loaded into the chamber the torque suddenly increases, then decreases to a low value. As the fusion of the polymer starts the torque increases. Later in this stage in consequence of the material temperature increase, the viscosity of the melt and the torque slightly decreases again. Due to crosslinking the viscosity and torque increases in the third phase but also the mechanical degradation of the polymer occurs and becomes dominating after the second maximum. In this particular case fragmentation starts prior to the gel point.

Although one can not expect that the original assumptions of CHARLESBY and PINNER are fulfilled, even in this case closely linear $s+\sqrt{s}$ vs. $1/t$ plots were observed (Fig.4). The rate of scission is comparable to that of crosslinking.

According to our observations oxygen does not play an essential role during dynamic tests (PUKÁNSZKY et al., in print), thus scission is caused rather by mechanical forces (shear) than by oxidative processes. The rate of crosslinking is much higher than expected from the static tests, the higher temperature in the mixing chamber would suggest 2-3 fold rate increase, but the crosslinking rate ($v_g = 2.2 \cdot 10^{-5}$ min^{-1}) was more than 10 times higher than that in pure thermal degradation and about 6 times of that in pure oxygen in static test at 180°C.

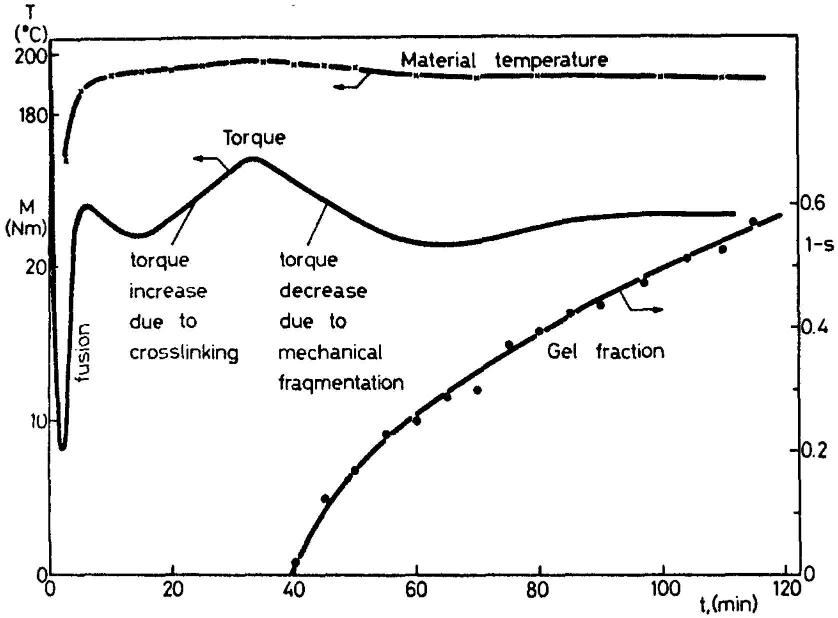


Figure 3. Gel formation (1-s) torque (M) and the material temperature (T) in the dynamic test. (Sample 10, set temp. 180°C 20 rpm, 60 g)

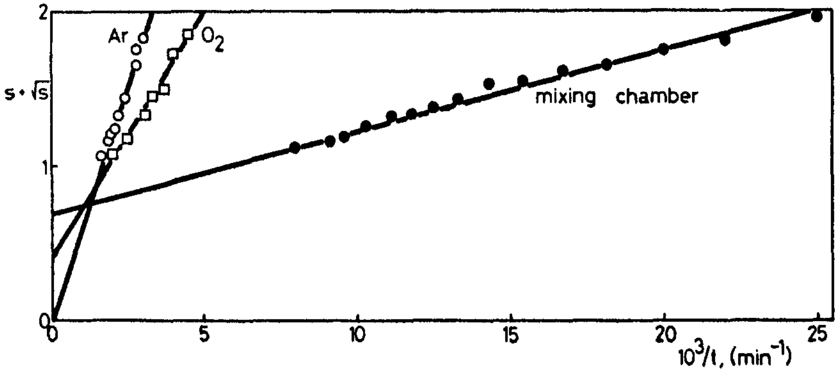


Figure 4. Comparison of Charlesby-Pinner plots of sample 10 under various conditions, at 180°C. (In the mixing chamber the actual temperature was higher)

References

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

ARLMAN, E.J., J.Polym. Sci. 12, 547 (1954)

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

CHARLESBY, A. and PINNER, S.H., Proc. Roy. Soc., A249, 367 (1959)

HUISGEN, R., DAHMEN, A. and HUBER, H., Am. Chem. Soc. 89, 7130 (1967)

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

IVÁN, B., NAGY, T.T., KELEN, T., TURCSÁNYI, B. and TÜDŐS, F., Polymer Bulletin, 2, 83 (1980)

KELEN, T., J.Macromol. Sci. Chem. 12, 349 (1978)

KELEN, T., IVÁN, B., NAGY, T.T., TURCSÁNYI, B., TÜDŐS, F. and J.P. KENNEDY, Polymer Bulletin, 1, 79 (1978)

LATTIMER, R.P. and KROENKE, W.J., J.Appl. Polym. Sci. 25, 101 (1980)

MARVELL, E.N., SEUBERT, J., VOGT, G., ZIMMER, G., MOY, G., SIEGMANN,J.R., Tetrahedron 34, 1323 (1978)

NAGY, T.T., KELEN, T., TURCSÁNYI, B. and TÜDŐS, F. 10th Anniversary Meeting of the Macromolecular Committee of the Hungarian Academy of Sciences Budapest, Nov. 1973

NAGY, T.T., C.Sc. Thesis, Hungarian Academy of Sciences 1976

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

NAGY, T.T., KELEN, T., TURCSÁNYI, B. and TÜDŐS, F., Polymer Bulletin 2, 77 (1980)

NAGY, T.T., IVÁN, B., TURCSÁNYI, B., KELEN, T. and TÜDŐS, F., 7th IUPAC Discussion Conference, Polymer Networks, Karlovy Vary Sept. 1980. Preprint No C44

O'MARA, M.M., Pure Appl. Chem. 49, 649 (1977)

PUKÁNSZKY, B., NAGY, T.T., KELEN, T. and TÜDŐS, F., under publication in J.Appl. Polym. Sci.

RASUVAEV, G.A., TROITSKAYA, L.S., MYAKOV, V.N. and TROITSKII, B.B., Dokl. Akad. Nauk. SSSR. Ser. Chim. 170, 1342 (1966)

STARNES, W.H. Jr. and EDELSON, D., Macromolecules 12, 797 (1979)

STARNES, W.H. Jr., in Developments in Polymer Degradation Vol 3, Ed. N.Grassie, Appl. Sci. Publ. London, in print

SVĚTLY, J., LUKÁS, R., MICHALCOVA, J. and KOLINSKY, M., Makromol. Chem. Rapid Comm. 1, 247 (1980)

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

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

Received November 22 / Accepted November 25, 1980