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Abstract

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ON THE MECHANISM OF CROSSLINKING OF POLYMER CHAINS UNDER THE ACTION OF GAMMA RADIATION

When a γ-quantum interacts with a molecule, an electron is knocked out from one of its orbits and, consequently, a positive ion is formed. When the ion is discharged by a thermal electron, highly excited molecules are formed, which decompose with the formation of free radicals. Consequently, the formation of transverse bonds must be connected with the occurrence of secondary processes involving radicals.

A study of the kinetics of the crosslinking process has shown that the rate of the process is constant in time and proportional to the radiation intensity to the first power. The simplest assumption about the mechanism of crosslinking is the assumption that the formation of transverse bonds during radiolysis occurs as a result of recombination of polymer radicals formed upon rupture of C–H bonds, and also as a result of addition of polymer radicals to double bonds of polymer molecules. The rate of crosslinking in this case will obviously be equal to

$$v = k_1 n^2 + k_2 n A$$

(n and A are the concentrations of radicals and double bonds, respectively). This scheme leads to the experimentally observed relations only when $n = \text{const}$ and $A = \text{const}$.

Accumulation of double bonds in the polymer during irradiation indicates that a steady state with respect to the concentrations of double bonds and free radicals is not reached. The constancy of the rate of crosslinking in time, therefore, indicates the insignificant role of the reactions of radical recombination and radical addition to double bonds, which is apparently associated with the extremely low rates of diffusion of polymer molecules in a solid polymer.

To understand the mechanism of the processes leading to the formation of transverse bonds, it is necessary to consider the radical reactions occurring in the irradiated polymer, in particular reactions involving atomic hydrogen.

Atomic hydrogen, formed as a result of rupture of a C–H bond of the polymer molecule under the action of radiation, possesses increased energy at the initial moment. This atom can either lose its excess energy or react according to one of the reactions given below:

1. Interaction with another hydrogen atom

$$H + H \rightarrow H_2 \tag{1}$$

2. Interaction with free radicals formed during irradiation

$$\sim CH_2\text{—}\dot{C}H\text{—}CH_2 \sim +H \begin{cases} \rightarrow \sim CH_2\text{—}CH_2\text{—}CH_2 \sim, \\ \rightarrow \sim CH_2\text{—}CH = CH \sim +H_2 \end{cases} \tag{2}$$

3. Interaction with double bonds

$$\sim CH_2\text{—}CH = CH \sim +H \rightarrow CH_2\text{—}\dot{C}H\text{—}CH_2 \sim . \tag{3}$$

4. Abstraction of a hydrogen atom from a polymer molecule

$$\sim CH_2\text{—}CH_2\text{—}CH_2 \sim +H \rightarrow \sim CH_2\text{—}\dot{C}H\text{—}CH_2 \sim +H_2. \tag{4}$$

The rates of reactions involving a "hot" hydrogen atom will be determined not so much by the magnitudes of the activation energies of these reactions as by the probability of collision of the hydrogen atom with one or another grouping. In carbocyclic polymers the concentration of CH_2 groups is several orders of magnitude higher than the concentrations of H atoms, free radicals, or double bonds and, consequently, the "hot" hydrogen atom will react predominantly by reaction (4), with formation of a polymer radical in the immediate vicinity of the site of rupture of the C–H bond. Recombination of such closely situated primary radicals and radicals formed by reaction (4) leads to the formation of cross-links. The rate of cross-linking by this mechanism, evidently, does not depend on the temperature of the specimen.

Reactions involving atomic hydrogen that has "lost" its excess energy will obey the usual laws. The rates of diffusion of gases in polymers are comparatively small, and therefore, taking into account that the concentrations of radicals and C=C bonds in them under irradiation are very low, in polymers of the polyethylene type "cold" hydrogen atoms will react mainly by reaction (4).

Radicals formed by reaction (4), which proceeds with the participation of "cold" hydrogen atoms, will be able to recombine with primary radicals only at a comparatively small distance from the site of formation of the H atom. The

Figure 1

Figure 1: Figure 1

rate of cross-linking in this case will evidently depend on the temperature of the specimen, since an increase in temperature will lead, on the one hand, to an increase in the probability that reaction (4) will proceed at small distances from the site of rupture of the C–H bond, and, on the other hand–owing to an increase in the mobility of the polymer chains–to the involvement in the radical-recombination reaction of radicals formed at comparatively large distances from the site of location of the primary radical.

The abstraction of a hydrogen atom from a polymer chain (reaction (4)) is coupled with the transition of the corresponding segment of the chain from a tetrahedral configuration to a planar one. In the case of polymers this transition is associated with displacement of segments of the polymer chains, which should lead to an increase in the activation energy of the reaction (as compared with the activation energies of analogous reactions in the case of low-molecular compounds). A particularly strong increase in the activation energy, and consequently a decrease in the rate of cross-linking, should be observed on passing to a glassy polymer.

As is seen from Fig. 1, the rates of cross-linking of polyethylene and polyvinyl chloride at temperatures below the glass-transition temperature T_c (respectively, −80 and +80°) are practically independent of temperature, i.e., in this case "cold" hydrogen atoms practically do not participate in reactions leading to the formation of cross-links. At temperatures above T_c the rate of cross-linking increases with temperature ("cold" hydrogen atoms are involved in the cross-linking reaction).

In a glassy polymer "cold" hydrogen atoms must also participate in reaction (4); however, the radicals formed in this process, because of steric hindrance, cannot recombine with the primary radical and remain in the polymer in a "frozen"state. As a result, upon holding polystyrene specimens irradiated at room temperature ($T_c = 80°$) or polyvinyl chloride specimens for some time at 90–100°, additional cross-linking is observed (Table 1). Heating polystyrene at a higher temperature (140–145°) leads to a decrease in the degree of cross-linking; the reasons for this decrease will be considered below.

The abstraction of a hydrogen atom from a side group (methyl, isopropyl, etc.) is not associated with displacement of segments of polymer chains in the transition state and therefore has practically the same activation energy as the corresponding reactions in the case of low-molecular compounds; moreover, vitrification of the polymer should not influence the rate of this reaction. Therefore, in polymers containing a sufficiently large

the number of such groups, "cold" hydrogen atoms will take part in cross-linking reactions even below the glass-transition temperature.

Figure 2

Figure 2: Figure 2

Fig. 1. Effect of temperature on the rate of cross-linking of polyethylene and polyvinyl chloride under irradiation with γ-radiation. *a*—polyethylene, 35 Mr; *b* —polyvinyl chloride, 24 Mr. The number of cross-links (in arbitrary units) was calculated from data on the swelling of samples in toluene (polyethylene) and dichloroethane (polyvinyl chloride). V and V_{-192° are the cross-linking rates at temperatures t and -192°, respectively.

Fig. 2. Effect of temperature on the rate of cross-linking of a polymer of structure $\left(\text{—}C_3H_6\text{—}CH\text{—}\underset{|}{CH_3}\right)_n$ (a) and on the rate of formation of trans-vinylene double bonds (absorption in the region of 964 cm^{-2}) (b). The cross-linking rates were calculated from data on swelling in toluene. V and V_{-192° are the cross-linking rates at temperatures t and -192°, respectively.

In order to test this assumption, the action of γ-radiation was investigated on polymers of structure $\left(\text{—}C_3H_6\text{—}CH_2\text{—}\underset{|}{CH_3}\right)_n$, obtained by decomposition of a mixture of diazomethane and diazoethane in the presence of $B(OCH_3)_3$.

Table 1

Effect of heating on the degree of cross-linking of irradiated polymers. $t_{irr} = 25^\circ$

Dose, Mr	Subsequent treatment	l_0/l**	$n_{heated}/n_{unheated}$	*Note
Polyvinyl chloride	**Polyvinyl chloride**	**Polyvinyl chloride**	**Polyvinyl chloride**	**Polyvinyl chloride**
98	Without heating	0.613	1.76	Additional cross-linking
98	Heating 4 hours at 90°	0.685		
Polystyrene	**Polystyrene**	**Polystyrene**	**Polystyrene**	**Polystyrene**
185	Without heating	0.334	1.56	Additional cross-linking
185	Heating 4 hours at 75°	0.365		

Dose, Mr	Subsequent treatment	l_0/l**	$n_{\text{heated}}/n_{\text{unheated}}$*	Note
204	Without heating	0.353	0.662	Decrease in the degree of cross-linking
204	Heating 4 hours at 140°	0.325		
195	Without heating	0.340	0.400	Decrease in the degree of cross-linking
195	Heating 2 hours at 145°	0.283		
225***	The sample is soluble			A gel fraction is formed

* The number of cross-links n (in arbitrary units) was calculated from data on the degree of swelling V of the sample according to the equation $n_{\text{heated}}/n_{\text{unheated}} = (V_{\text{unheated}}/V_{\text{heated}})^{5/3}$; the subscripts heated and unheated denote, respectively, heated and unheated samples. Swelling of polyvinyl chloride was in dichloroethane, and of polystyrene in toluene.
** l_0/l is the ratio of the length of the original sample to the length of the swollen irradiated sample.
*** Irradiation temperature 130–135°.

High cross-linking rates of this polymer in the glassy state ($T \approx -80°$), 2.5 times exceeding the cross-linking rate of polymethylene under these conditions, and the constancy of the cross-linking rate in the temperature interval

temperatures of −190 to +35° indicate that in polymers of this type not only "hot" but also "cold" hydrogen atoms are practically completely captured at a very short distance from the site of formation of the primary radical.

An increase in the crosslinking rate by a factor of 2.7 is also observed when isopropyl groups are introduced into the para position in polystyrene (by treating polystyrene with isopropyl chloride in the presence of $AlCl_3$ (Table 2)). The high rates of reaction (4) in the case of polymers containing side groups are also evidenced by the fact that heating irradiated isopropylated polystyrene, which was irradiated in the glassy state, at a temperature above T_c does not lead to additional crosslinking (Table 3).

Table 2

Effect of side groups on the rate of crosslinking of polymers. $t_{irr} = 25°$

Dose, Mr	Polymer	l_0/l^*	n_{IPPS}/n^{**}_{PS}
200	Polystyrene	0.345	
200	Isopropylated polystyrene	0.422	2.74

* See note to Table 1.
** n is the number of crosslinks (in arbitrary units). The subscripts PS and IPPS denote, respectively, polystyrene and isopropylated polystyrene.

Upon irradiation of copolymers of the type

$$\left(\begin{array}{c} -C_3H_6 - CH_2- \\ \qquad\qquad | \\ \qquad\quad CH_3 \end{array} \right)_n$$

at 35–100°, a sharp decrease in the crosslinking rate is observed, accompanied by an increase in the rate of accumulation of trans-vinylene double bonds (estimated from absorption in the region of 964 cm^{-1}) (Fig. 2). This effect is apparently associated with the occurrence of a chain-transfer reaction, as a result of which radicals of the isopropyl type are converted into tert-butyl radicals. The latter, on interacting with radicals of the isopropyl type, disproportionate to a considerable extent ([1]), which leads to a decrease in the crosslinking rate and to an increase in the rate of accumulation of double bonds in the polymer.

Table 3

Effect of heating on the degree of crosslinking of irradiated isopropylated polystyrene, $t_{irr} = 25°$

Dose, Mr	Subsequent treatment	l_0/l^*	n_h/n^*_{irr}
204	Without heating	0.410	1.0
204	Heating for 4 hours at 100°	0.414	

* See note to Table 1.

The literature ([2]) contains data indicating that upon irradiation of isotactic polypropylene, not crosslinking but destruction of the polymer molecules occurs. However, this conclusion is most probably erroneous. The decrease in molecular

weight is apparently associated not with radiation-chemical but with thermal degradation of the polymer, occurring when the sample is heated to ~150° during determination of its molecular weight. Similar results were obtained by us when polystyrene irradiated at room temperature was heated to 140–145°, or when polystyrene was irradiated at 135°. The data given in Table 1 show that, whereas heating the sample at 90–95° increases the degree of crosslinking, heating at 140–145° noticeably decreases it. The results obtained give grounds for believing that the determining event in the processes of thermal degradation of polymers is the formation of a free radical within the chain.

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Note: Figure translations are in progress. See original paper for figures.