# Reactions of Hydrogen Atoms with Polymers at Low Temperatures*

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The present paper demonstrates that the polymers of different chemica structure interact at 100—150 K with atomic hydrogen, free radicals being formed. Macromolecules which contain aromatic rings (PS, PMS and PET) or nitrile groups (PAN) join hydrogen atoms. In other polymers (PE, PP, PI, PEO, PVA, PAA, PMM, PCL, and PVAc) the abstraction of hydrogen atoms, generally from chief polymer chains, is observed.

The reactions of atomic hydrogen with polymers take place in thin surface layer. The thickness of this layer is about $10^{-6}$ cm. The local radical concentrations attain $1-5 \times 10^{19}$ spins $g^{-1}$.

The values of activation energy of hydrogen atom abstraction from macromolecules at low temperatures are very small. Thus the activation energy for hydrogen atom abstraction from PI is $2 \pm 0.5$ kcal mole$^{-1}$ and $1.2 \pm 0.5$ kcal mole$^{-1}$ for PEO.

By interaction of hydrogen atoms with different organic compounds at low temperatures free radicals arise which may be observed by e.s.r. method [1—4]. Literature data related mainly to the compounds with low molecular weight, and reactions of atomic hydrogen with macromolecules have scarcely been studied. There are only some data about reactions of atomic hydrogen with polystyrene and substituted polystyrenes [5—7] and some biopolymers [8, 9].

In this work we have attempted to study reactions of hydrogen atoms with the polymers of different chemical structure. The attention has mostly been paid to the determination of the structure of free radical reaction products and the kinetic peculiarities of reactions.

The reactions have proceeded in cavity of e.s.r. spectrometer, the mixture of atomic and molecular hydrogen being pumped through polymer samples.

There has been studied the interaction of atomic hydrogen with polymers: polyethylene (PE), polypropylene (PP), polyisobutylene (PI), poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMM), poly(vinyl acetate) (PVAc), poly(acrylic acid) (PAA), polyacrylonitrile (PAN), polystyrene (PS), poly(α-methyl styrene) (PMS), poly(ethylene terephthalate) (PET) and polycaprolactam (PCL).

The temperature during reactions has been in the range 100—150 K.

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## Experimental

Hydrogen atoms were produced by high-frequency electrodeless discharge. The discharge was initiated with high-frequency generator (13.56 MHz). The discharge quartz tube (diameter 12 mm) possessed two bends in order to exclude the action on the samples of the ultraviolet radiation, produced in the discharge. The reaction tube (diameter 9 mm) was made of a thin-wall quartz and had a supporting disk (with orifice), on which the polymer samples were placed. The distance between the discharge and the reaction zones was about 20 cm. In order to prevent the recombination of hydrogen atoms on walls the tubes were carefully washed and treated with concentrated hydrofluoric acid before experiments.

The reaction tube was placed in the cavity of the e.s.r. spectrometer (type IChF-2), so we had the opportunity to observe the formation of macroradicals and to check the concentration of hydrogen atoms at the same time. The atomic hydrogen concentration in the reaction zone was $10^{13}-10^{14}$ cm$^{-3}$, depending on the experimental conditions. The reaction tube was thermostatted with the flow of nitrogen gas from the closed Dewar vessel.

Before starting the experiments the polymer was pumped down to a pressure of $10^{-3}-10^{-4}$ mmHg, then the thermostatting system was set working and the sample was maintained at the needed temperature. Hydrogen was introduced into the system (the pressure about 1 mmHg) and the discharge was switched on.

The commercial hydrogen was used without further purification.

PE, PP, and PEO were obtained at our institute by the polymerization of the monomers on proper catalysts.

PAA was prepared by photopolymerization of acrylic acid at room temperature, unreacted monomer being evacuated.

PMS was obtained in Karpov's Physico-Chemical Institute with $Li(C_2H_5)$ catalyst; it was reprecipitated from benzene solution by methanol.

Other polymers were commercial products. PI was reprecipitated from its benzene solution by ethanol. PVAc was precipitated from methanol solution by water. PMM was reprecipitated twice from benzene by ethanol.

The depth of the penetration of hydrogen atoms into polymers is limited [5, 10—12]. That is why the polymer samples with large specific area were prepared. Usually the polymers were ground in vibromill [13] at 100 K, and powder samples were transferred

*Table 1*

Characteristics of polymer samples

| Designation of samples | Method of preparing | $m^*$ (g/g) | Specific area $S$ [m$^2$ g$^{-1}$] |
|---|---|---|---|
| PI | thin polymer layers on $SiO_2$ | 0.15 | 126 |
| PVAc-1 | | 0.15 | 160 |
| PVAc-2 | | 0.45 | 84 |
| PVAc-3 | | 0.90 | 40 |
| PVAc-4 | | 1.50 | 32 |
| PEO | | 0.15 | 165 |
| PVAc-5 | ground in vibromill | | 2 |
| PMM | fluff | | 5 |

* Quantity of polymer on $SiO_2$.

to the reaction tube immediately after forming a dispersion. From some polymers there were prepared fluffs by freeze-drying benzene solutions [14, 15]. In order to get samples with very large specific area some polymers were deposited in thin layers on the surface of $SiO_2$ (Aerosil-175) with the specific area of 170 m². In such way there were prepared the samples PI, PEO, PVAc-1, PVAc-2, PVAc-3, and PVAc-4. 1% solutions of these polymers in carbon tetrachloride or benzene were shaken with $SiO_2$ at room temperature during 6 hours, then the solvents were evaporated *in vacuo*. Table 1 contains the characteristics of some polymer samples.

For measuring the specific area of samples the chromatographic method of thermodesorption of argon [16] was employed.

## Results and Discussion

The macroradicals have been produced in all the studied polymers at 100—150 K. Their formation cannot be assigned in no case to the action of u.v. radiation, generated in the discharge. In check experiments made in tubes which had not been previously treated, neither hydrogen atoms, nor macroradicals were observed. Thus macroradicals are formed only as a result of the interaction of atomic hydrogen with polymers.

In Fig. 1 there are shown the e.s.r. spectra of some macroradicals. There was made a detailed examination of isotropic hyperfine structure in accordance with half empiric rules for analysis of e.s.r. spectra [17]. In most cases the structure of the free radical intermediates of reactions was established. In some cases the special experiments with deuterium instead of hydrogen were made. The parameters of e.s.r. spectra and the supposed structure of macroradicals are given in Table 2.

In PS, PMS, and PET the spectra are triplets, the distance between outmost lines being in all spectra 86—90 G. The intensity ratio of components is close to 1 : 2 : 1. The e.s.r. signals in these polymers are due to the cyclohexadienyl type radicals which are produced as a result of hydrogen atom addition to aromatic ring [3, 5—7].

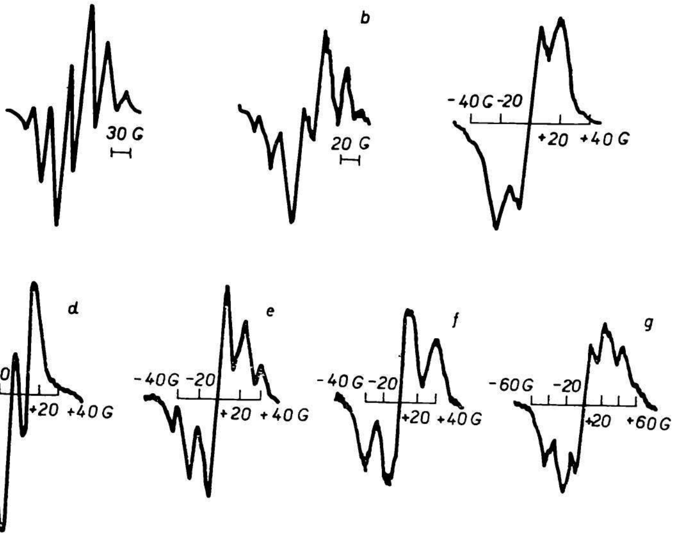
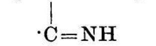


*Fig. 1.* The e.s.r. spectra of macroradicals formed at 140 K in PE (*a*); PP (*b*); PEO (*c*); PMM (*d*); PAA (*e*); PVA (*f*); PCL (*g*).

*Table 2*

The structure of macroradicals formed at the exposure of polymers to hydrogen atoms

| Polymer | Spectra e.s.r. | | Macroradical structure |
|---|---|---|---|
| | number of lines | total splitting [G] | |
| PE | 6 | 154 | $-CH_2-\dot{C}H-CH_2-$ |
| PP | 6 | 130 | $-CH_2-\dot{C}(CH_3)-CH_2-$ |
| | | | $-CH_2-CH(\dot{C}H_2)-CH_2-$ (?) |
| PI | 2 | 22 | $-C(CH_3)_2-\dot{C}H-C(CH_3)_2-$ |
| PMM | 2 | 21 | $-C(CH_3)(COOCH_3)-\dot{C}H-C(CH_3)(COOCH_3)-$ |
| PEO | 3 | 36 | $-CH_2-O-CH_2\dot{C}H-O-CH_2-$ |
| PVA | 3 | 62 | $-CH_2-\dot{C}(OH)-CH_2-$ |
| PVAc | 5 | 75 | $-CH_2-\dot{C}(OCOCH_3)-CH_2-$ |
| PAN | 7 | 138 |  $-CH_2-\underset{\cdot C=NH}{\underset{\vert}{CH}}-CH_2-$ |
| | | | $-CH_2-\dot{C}(CN)-CH_2-$ |
| PAA | | 86 | $-CH_2-\dot{C}(COOH)-CH_2-$ |
| | | | $-CH_2-\dot{C}(COOH)-CH(COOH)-$ (?) |
| PCL | 5 | 75 | $-CO-NH-\dot{C}H-CH_2-$ |
| PET | 3 | 86 | $-CH_2-COO-\dot{C}_6H_5-COO-CH_2-$ |
| PS | 3 | 90 | $-CH_2-CH(\dot{C}_6H_6)-CH_2-$ |
| OPMS | 3 | 88 | $-CH_2-C(CH_3)(\dot{C}_6H_6)-CH_2-$ |

The e.s.r. signal of radicals in PAN is very complex and consists of 7 lines. The comparison of spectra observed during the action on PAN of hydrogen and deuterium atoms showed that the reaction took place in two ways: the addition of hydrogen atom to $C{\equiv}N$ bond and the abstraction of hydrogen atom from the polymer chain. The dominant reaction is the addition of hydrogen atom.

The spectra in PE, PI, PMM, PVA, and PCL indicate the presence of the macroradicals with free valency in the middle of polymer chain (Table 2), which arise as a result of hydrogen atom abstraction from macromolecules. In PP, PAA, and PVAc the reaction of hydrogen atom abstraction also proceeds but the structure of macroradicals formed is not definitely established.

The concentration of the arising macroradicals depends on many factors: polymeric structure, temperature, concentration and duration of action of atomic hydrogen, specific area of samples. It should be noted that isotropic hyperfine structure of e.s.r. spectra is usually poorly resolved and line width increases with the growth of radical concentration. This fact and the dependence of average radical concentration on specific area of sample show that hydrogen atoms reactions with polymers take place in thin surface layer and the local concentrations of macroradicals in this layer are very high. In order to estimate the thickness of this layer and to measure the local radical concentrations the run of experiments was carried out with polymers deposited in thin layers on silica.

In Fig. 2*a* there is presented the dependence of radical yields at 120 K on the exposure time for series of PVAc samples (see Table 1). The concentration of atomic hydrogen in all experiments was constant and equal to $5 \times 10^{14}$ cm$^{-3}$. This figure shows that the maximum radical concentrations ($R_{\mathrm{lim}}$) for samples PVAc-1, PVAc-2, and PVAc-3 ($S \geqslant 40$ m$^2$ g$^{-1}$) are close to each other and reach $10^{19}$ spins g$^{-1}$. $R_{\mathrm{lim}}$ for PVAc-4 is twice less. Fig. 2*b* shows the dependence of maximum radical concentration in PVAc on specific area of samples. The point in curve beginning corresponds to $R_{\mathrm{lim}}$ in the powdered sample PVAc-5. It appears from Fig. 2*b* that the maximum radical concentration stopped depending on the specific area at $S = 40$ m$^2$ g$^{-1}$. In other words, in the samples with $S \geqslant 40$ m$^2$ g$^{-1}$ all the layer of deposited polymer "works". If the thickness of such layer is $\delta$ its volume is $1/\varrho = S\delta$, where $\varrho$ is PVAc density $= 1.18$ g cm$^{-3}$. Then $\delta = 2 \times 10^{-6}$ cm.

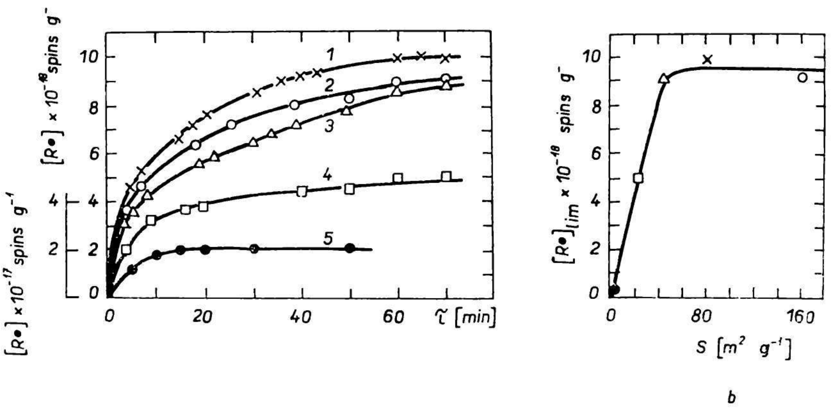


*Fig.* The results of the experiments with PVAc at 120 K.
*a*) The yield of macroradicals *vs.* the exposure time.
*1.* PVAc-2; *2.* PVAc-1; *3.* PVAc-3; *4.* PVAc-4; *5.* PVAc-5 (ordinate $R \times 10^{-17}$ spins g$^{-1}$).
*b*) The dependence of maximum radical concentration on specific area of samples.

The lower values of $R_{\mathrm{lim}}$ (in comparison with $10^{19}$ spins g$^{-1}$) in PVAc-4 and PVAc-5 are due to the limited penetration of hydrogen atoms into these samples. One can estimate the value $\delta$ by means of equation $R_{\mathrm{av}} = R_{\mathrm{loc}}\, S\delta$, where $R_{\mathrm{loc}} = 10^{19}$ spins g$^{-1}$. Then $\delta = R_{\mathrm{av}}/R_{\mathrm{loc}}\, S\varrho = (1/1.18 \times 10^{19}) \times R_{\mathrm{av}}/S$. The $\delta$ values for samples PVAc-4 and PVAc-5 are $1.3 \times 10^{-6}$ cm and $0.9 \times 10^{-6}$ cm, respectively.

Thus the depth of hydrogen atoms penetration into PVAc is $1-2 \times 10^{-6}$ cm and the local concentrations are $10^{19}$ spins g$^{-1}$. In other polymers deposited on silica (PI, PEO) maximum radical concentrations reach higher values ($5 \times 10^{19}$ spins g$^{-1}$).

From the dependence of radical yield on the exposure time the kinetic parameters of reactions of hydrogen atoms with macromolecules may be measured

$$\mathrm{d}R/\mathrm{d}t = k_1[\mathrm{H}\cdot]\,[\mathrm{P}] - k_2[\mathrm{H}\cdot]\,[\mathrm{R}\cdot] = k_3[\mathrm{R}\cdot]^2, \tag{1}$$

where $[\mathrm{H}\cdot]$ — concentration of atomic hydrogen,
$[\mathrm{P}]$ — concentration of macromolecular units,
$k_1, k_2, k_3$ — the rate constants of reactions of hydrogen atoms with polymer ($k_1$), hydrogen atoms with radicals ($k_2$) and recombination and disproportionation of radicals ($k_3$).

In general the value [H•] depends on diffusion coefficient of hydrogen atoms into polymers. In samples PI, PEO, and PVAc-1 the polymer quantity deposited on silica is 0.15 g/g, what is near to one molecular layer, and in such thin layers reaction is not diffusion controlled. At the beginning of the process [R•] values are very small and $dR/dt \cong k_1[H\bullet]\,[P]$.

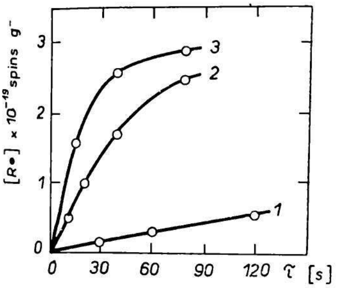


*Fig. 3.* The rate of radical formation in PI, deposited on silica at temperatures: *1.* 99 K; *2.* 123 K; *3.* 145 K.

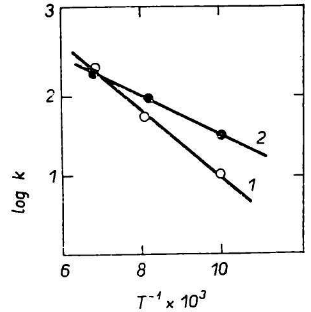


*Fig. 4.* The rate constants of abstraction reaction of hydrogen atom (in relative units) as a function of the reciprocal of temperature. *1.* PI; *2.* PEO.

In Fig. 3 the rates of radical formation in PI at three temperatures are presented. From initial linear parts of curves the values of the rate constants of hydrogen atom abstraction (in relative units) were calculated. Fig. 4 shows the temperature dependence of this constant. Analogous experiments were made with PEO and Arrhenius plot for this polymer is also presented in Fig. 4. The data in Fig. 4 yield activation energies for reaction of hydrogen atom abstraction from PI and PEO. They are 2 and 1.2 ± 0.5 kcal mole$^{-1}$.

## References

1. Cole T., Heller H. C., *J. Chem. Phys.* ***42***, 1668 (1965).
2. Chachaty C., Shmidt M. C., *J. Chim. Phys.-Chim. Biol.* ***62***, 527 (1965).
3. Shatrov V. D., Chkheidze I. I., Shamshiev V. N., Buben N. Ya., *Khim. Vys. Energii* ***2***, 413 (1968).
4. Shatrov V. D., Chkheidze I. I., Shamshiev V. N., Buben N. Ya., *Dokl. Akad. Nauk SSSR* ***181***, 376 (1968).
5. Ingalls R. B., Wall L. A., *J. Chem. Phys.* ***35***, 370 (1961).
6. Wall L. A., Ingalls R. B., *J. Chem. Phys.* ***41***, 1112 (1964).
7. Tiedeman G., Ingalls R. B., *J. Phys. Chem.* ***71***, 3092 (1967).
8. Herak J. N., Gordy W., *Proc. Nat. Acad. Sci. USA* ***55***, 1373 (1966).
9. Liming F. G., Gorgy W., *Proc. Nat. Acad. Sci. USA* ***60***, 794 (1968).
10. Klein R., Sheer M. D., *J. Phys. Chem.* ***62***, 1011 (1958).
11. Ingalls R. B., Hardy J. R., *Can. J. Chem.* ***38***, 1734 (1960).
12. Henriksen T., *J. Chem. Phys.* ***50***, 4653 (1969).

13. Abagyan G. V., Butyagin P. Yu., *Biofizika* ***9***, 180 (1964).
14. Lewis F. M., Mayo F. R., *Ind. Eng. Chem., Anal. Ed.* ***17***, 134 (1945).
15. Vinogradov G. V., Titkova L. V., *Vysokomol. Soedin.* ***IIA***, 951 (1969).
16. Buyanova N. E., Karnaukhov A. P., *Opredelenie udelnoi poverkhnosti tverdykh tel khromatograficheskim metodom teplovoi desorbtsii argona. (Determination of Specific Area of Solid Substances by Means of Chromatographic Method of Thermal Desorption of Argon.)* Nauka, Sibirskoe otdelenie, Novosibirsk, 1965.
17. Butyagin P. Yu., Dubinskaya A. M., Radtsig V. A., *Usp. Khim.* ***28***, 593 (1969).