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# Chemical Modification of Fiber-forming Polymers Based on Recombination Addition Reactions

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The essence of chemical modification processes of fiber-forming polymers based on recombination addition reactions involves preliminary sorption of low-molecular components by the fiber being in a high elasticity state with the subsequent transfer of interacting substances into a free radical state as a result of chemical or radiation initiation. Recombination of activated parts then leads to the fixation of a low-molecular component in a polymer matrix.

Various versions of these reactions based on modifications of fibrillar proteins (fibroin and keratin), polyamides, cellulose and its esters, polyvinyl alcohol with ionogenic (cationic and anionic) and non-ionogenic (disperse) dyes of different classes have been considered.

**KEY WORDS** Fibers, chemical modifications, addition reactions.

## INTRODUCTION

At present extensive experimental and theoretical data on chemical modifications of linear high-molecular compounds have been accumulated. The problem has aroused interest due to great possibilities in modifying initial structures of polymer substrates and as a result in changing physical-chemical and structural properties of fiber-forming polymers. Naturally, it predetermines the possibility for obtaining various polymer materials with optimum consumable characteristics. It is known that chemical modifications of fiber-forming polymers is achieved by means of the modification of the initial structure of micromolecules due to:

- co-polymerization (or co-polycondensation)
- polymeranalogical transfers
- graftcopolymerization.

However, there is an alternative for achieving this aim which can be reasonably specified as a “recombination addition reaction.” The essence of this method consists in pre-sorption of a low-molecular component (modifying agent) by fibers or films being in the high elasticity state followed by transfer of interacting substances into a free radical state caused by the chemical or radiation initiation. Recombi-

nation, wherein free-radical centers are generated, leads to the formation of covalent bonds among them and as a result to the fixation of the modifying agent in the polymer substrate.

Experimental work carried out at various laboratories during the past 20 years proves the possibility and expedience of using these reactions for achieving practical objectives.

This article deals with studies of one of the variants of polymer chemical modifications, namely "fast" dyeing processes for natural and chemical fibers with dyes of different classes, including the dyes characterized by the absence of the polymer substrate affinity. Unfortunately, it is not possible to give all experimental and process details of the studies in such a small article.

## METHODICAL

Objects of study:

Natural silk (S):

Linear density, 4.5–5.0 tex

Sericine, 3.8%

Nitrogen, 18.4%

Merino wool, washed 64 k(W):

Linear density, 0.456 tex

Sulphur (total), 2.9% (weight)

Nitrogen, 16.5% (weight)

Polykapronemide textile yarn (PCA):

Linear density, 10/25 tex

Low-molecular fractions (LMF) 1.3–1.4% (weight)

Rayon (HC):

Linear density, 13.3/40 tex

Acetate textile yarn (AC):

Linear density, 16.6/39 tex

Bonded acetic acid, 54.3% (weight)

Polyvinylalcohol fiber (PVA):

Linear density, 0.450 tex

Purified dyes (dyeing agent content is given in brackets)

Cationic (basic):

Rodamine B (96.4%)

Rodamine R (94.7%)—II

Basic Brilliant Green (99.8%)—III

Auramine (95.5)—IV

Eosine (94.2%)—V

Basic Blue R (95.8%)—VI

Basic Violet R (98.1%)—VII

## Anionic (acid):

- Bright Blue (89.4)—VIII
- Metanilic Yellow (96.1%)—IX
- Scarlet (97.4%)—X
- Fast Yellow (96.7%)—XI
- Chromic Brown R (95.9%)—XII

## Non-ionogenic (disperse):

- Alizarine (98.7%)—XIII
- Violet R (959.2%)—XV
- Pink Y (58.6%)—XVI
- Yellow 6z (58.2%)—XVII
- Antracenic Blue (59.2%)—XVIII
- Red-Brown 2R—XX
- Bright Pink (58.3%)—XXI
- Blue Green (54.9%)—XXII
- Orange 2R (48.3%)—XXIII
- Red 2 B (51.4%)—XXIV

EPR-spectroscopic studies in the range of 77–298 K have been carried out with Spectrometer EPR-3 "SIBIR" and P-1301 using high frequency modulation of magnetic field. The spectra excluding signal saturation have been chosen.

The structure of original and modified polymers has been evaluated by electronic and UR-spectra, the element composition by the procedures: X-raying; sorption of water vapors, methanol and benzol at 298 K using Mc Ben's high vacuum apparatus; determination of fiber density in various fluids by electro-magnetic float [1]; DTA and TGA, DSC; birefringence,  $\Delta n$ ; optical and electronic microscopy. Physical-mechanical properties of the original and modified fibers have been specified by relative tenacity,  $\sigma_\alpha$ , elongation,  $\epsilon_\alpha$ , and the initial module,  $E_4$ .

Dyes, fixing fastness has been evaluated by:

- modified fiber resistance to various media: water (including SAS), acetone, dimethylformamide (DMF), pyridine, aguapyridine mixtures at room temperatures and during heating;
- isothermal kinetics of swelling and dissolving modified fiber;
- resedimentation of the modified polymer from the solutions with the following spectrophotometric analysis of the sediment;
- hydrolysis of the modified polymers with the following thinlayer chromatography of hydrolyzate;
- resynthesis of the dye in fiber—for the dyes containing azogroup [2].

## EXPERIMENTAL

Recombination addition reactions used for modifications of fiber-forming materials represent a variety of heterogeneous processes. However, their peculiar feature is a modification of active surfaces of fibers caused by swelling and transferring

polymer substrate into a high elasticity state. It is known<sup>3,4</sup> that the dyeing dynamics (modification in particular) is determined by dyes' diffusion in solutions, by sorption of its active surface of the fiber material, and by the diffusion of the dyeing substance in fiber. The process is accomplished by an interaction of dyes and polymer substrates. Kinetic and thermodynamic aspects of the dyeing process of NS with different ionogenic (X–IX) dyes in aqueous and non-aqueous (DMF, perchlorethylene) media; W—with ionogenic (I–XII) and non-ionogenic (XIV–XVI; XIX–XXII) dyes; PCA—with ionogenic (I–III), (IX–XI) and non-ionogenic (XII–XXIV) dyes; HC and PVA—with ionogenic (I, III, IX, XI) and non-ionogenic (XX, XXIII) and also with AC-non-ionogenic (XX, XXIII) dyes. Sorption isotherms of all studied dye classes within the temperature range of 293–370 K for NS, W, HC and PVA are satisfactorily described by Langmuir's equation<sup>4</sup>:

$$(C_B)^{-1} = k \cdot [S_a] \cdot (C_P)^{-1} + [S_a]^{-1},$$

where

$(C_B)$ —dye content (fiber)

$(C_P)$ —dye content (solution)

$[S_a]$ —dye "saturation" limit (polymer substrate).

Ionogenic dyes' sorption being isothermal,  $[S_a]$  from aqueous solutions is 10–100 times higher than from their solutions with aprotic solvents.

Studies of PCA dispersion as well as AC dyes' sorption processes have shown that sorption process can be precisely described by Freundlich's Equation<sup>5</sup>:

$$(C_{B,\infty}) = \nu \cdot (C_{P,\infty})^\kappa$$

where

$(C_{B,\infty})$  and  $(C_{P,\infty})$ —equilibrium content of the dye in fiber and in the dyeing bath respectively;

$\nu$  and  $\kappa$ —constants, where  $\kappa = 0.95–1.20$ .

It allows as a first approximation to describe the penetration process of disperse dyes into fiber as dissolution. Increased temperatures of dyeing and contents of the dyes in the dyeing bath results in sorption acceleration.

The conditions ensuring rather high sorption have been chosen for each "fiber-dye" system. Moreover, all fiber weight was evenly dyed, and microscopic colorimetric analysis of the fiber cross sections prove this. Dyeing takes place under conditions when the fiber swelling is limited and the polymer substrate subjected to disglassing.

Glassing temperature ( $T_g$ ) of the fiber-forming polymer is essentially reduced. The dyes added into the fiber-forming polymer cause additional plasticizing effect. The more this additional effect, the less the dyes' chemical affinity to the polymer substrate. Increased segmentary movement of the fiber-forming macromolecules contribute to much more uniform dye distribution in the fiber weight.

## REACTION INITIATION

Different variants of the recombination addition reactions based on chemical and radiation initiation have been studied.

Chemical procedures were based on the use of various peroxidates as well as on oxidation-reduction systems. Mino-Kaiserman's<sup>6</sup> reaction was also used for the initiation.

pH medium is critical (Figure 1) to initiating (activating) the fixing processes in aqueous media with non-organic peroxides ( $H_2O_2$ ;  $K_2S_2O_8$ ). Higher temperatures of the activation treatment from 333 up to 363 K result in increased fixation rates and quantity of dye attached to polymer.

During activation by oxidation-reduction systems [ $H_2O_2$ - $K_2S_2O_5$ ;  $Fe^{+2}$ ;  $K_2S_2O_8$ - $K_2S_2O_5$ ;  $HCOOH$ ] the reaction rate and efficiency are increasing. It should be noted that each "polymer-dye" pair is characterized by the optimum content of peroxide in the reaction medium as well as the reducing agent.

Coloristic features of the dyed fiber do not appreciably change after the fixation treatment carried out under optimum conditions. The dye quantity fastly fixed in S due to activation treatment is 60–85% for I–VII and 45–55% for VIII–IX.<sup>7–16</sup> Correlation of results achieved with the help of various structural anionic dyes for the fast dyeing of W<sup>12,13</sup> is of great interest. We had the following content of non-extractive dyes in W under similar conditions of dyeing and fixing in the presence of  $H_2O_2$  and  $pH = 3.6$ :

Dyes	Dyes' content, g · kg
IX	$5.4 \pm 0.3$
X	$0.79 \pm 0.23$
XI	$3.1 \pm 0.5$
XII	$5.9 \pm 0.6$

These differences are perhaps caused by specific features of chemical constitution

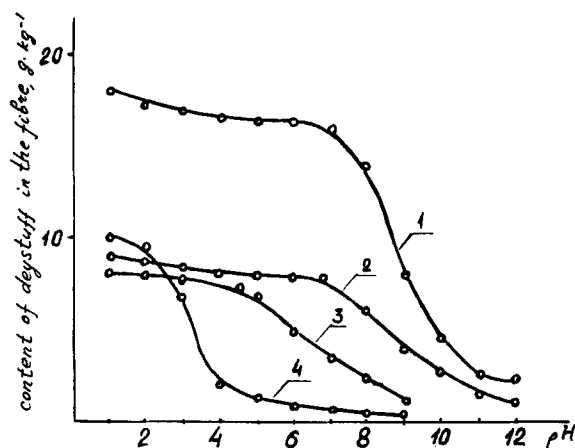


FIGURE 1 pH effect on the content of the dyes fixed in natural silk: 1.4—Rodamine B; 2.3—acid methyl yellow while initiating 1.2— $K_2S_2O_8$  and 3.4— $H_2O_2$ .

of these dyes; it seems that functional groups capable of transfer into a free radical form under the influence of "initiating" actions are missing in molecule X. The possibility of the initiation process based on Mino-Kaiserman's reaction was also studied.<sup>14</sup> With the help of S, HC, PVA and AC it was shown that fixation of the dyes containing H<sub>2</sub>N- and aliphatic HO groups was possible in this fiber.

Ce(4+), Mn(3+) and VO<sub>2</sub>(+1) compounds were used as oxidants, and hydroxy- and/or amino groups of dyes and polymer substrate served as reducing agents.

An effective method of dyes' fixation in polymer substrates is the radiation treatment of the dyed fiber being in a high elasticity state. It should be noted that a considerable increase in the uniformity of the coloristic effects obtained is achieved when PCA is exposed to beta doses.<sup>15</sup> Dose radiation influence on the fixation in S of cationic and anionic<sup>11,16,17</sup>; in W — ionogenic and non-ionogenic (Figure 2)<sup>18-21</sup> and in PCA — non-ionogenic (disperse) dyes<sup>22-24</sup> has been studied.

### GENERATION AND LOSS KINETICS OF FREE-RADICAL CENTERS IN FIBER-FORMING POLYMERS

EPR spectra studies of S have shown that the nature of the formation of free-radical centers by the chemical and radiation initiation is identical. Similar results have been obtained while studying EPR spectra of W and PCA. IR-spectroscopic study of S, W and PCA exposed to multiple treatments with peroxide solutions<sup>25-29</sup> (or by gamma irradiation, different doses) have shown that relative intensity of CH<sub>2</sub>-lines decrease as the reaction progresses.

It proves the essential role of the CH<sub>2</sub>-group in the generation process of free-radical centers, particularly when considering the possibility of the formation of glycolic radicals:

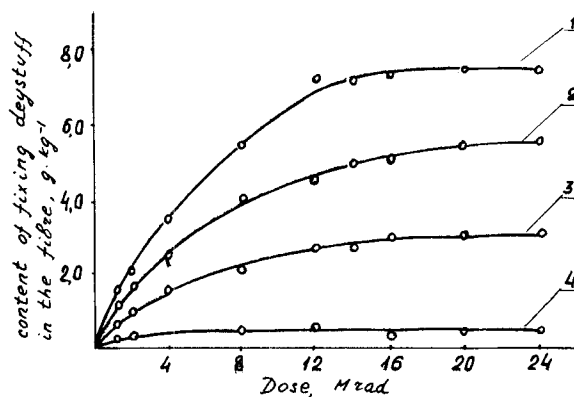
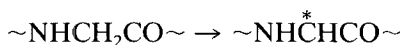
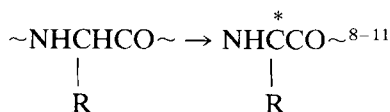
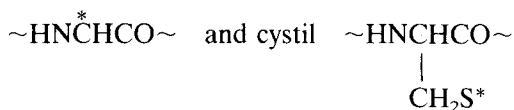


FIGURE 2 The influence of gamma-radiation dose on disperse dyes fixating in wool: 1—Disperse Violet R (XIV); 2—Disperse Red-Brown (XIX); 3—Disperse Yellow Fast 2R (XX); and 4—Disperse Yellow 6 z (XVII).

The probability exists that the free radical centers are generated on other links in accordance with the pattern



It was shown<sup>12,13</sup> that relative intensity of CH<sub>2</sub>-lines decreased during multiple treatment of W by peroxides as well as irradiation by doses of more than 5 Mrad.<sup>18-21</sup> At the same time the content of amino nitrogen and total sulfur in W decreased. Two basic types of free radical centers<sup>30</sup>:



appeared during chemical or radiation initiation of W. In addition it should be noted that a duplet form of the “glycil” signal was the most stable.<sup>31</sup>

The dynamics of free radical accumulation in undyed W was similar to the increase of the fixed dyes’ content when the dose was higher (Figure 3). Kinetics analysis of the free radical centers’ loss in W in atmosphere and under vacuum at different temperatures showed that the process total rate was on the order of 1.4–1.5 relative to their concentration. For S and PCA it increased up to 1.7–2.0 (Figure 4).

Certain generation features and the loss of free radical centers in PCA films (Figures 3 and 4) were systematically studied. Radicals’ radiation-chemical yield evaluated for the accumulation (initial) part of the kinetic curve (up to 3 Mrad) was ~2.8 sp. (100 e·V)<sup>-1</sup>. Apparent activation energy of radicals, ΔE<sub>i</sub> = 100 kJ·mol<sup>-1</sup> at 1.4 Mrad dose, and ΔE<sub>i</sub> = 85 kJ·mol<sup>-1</sup> at 9 Mrad. Free-radical

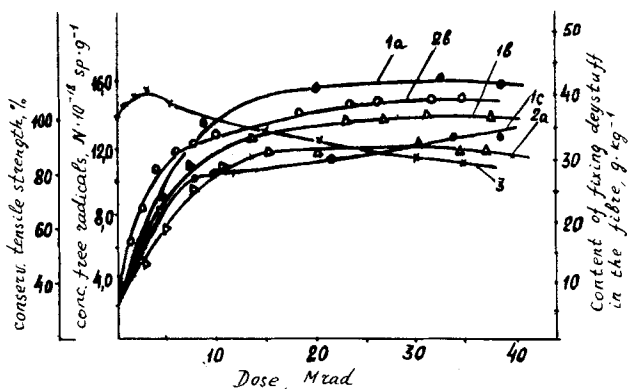


FIGURE 3 Dose relationship on some parameters of gamma-irradiation in raw and dyed fibers. 1. Accumulation dynamics of free radicals in: a) wool; b) natural silk; c) polykapronamide yarn. 2. Content of fixed dyes in wool: a) disperse blue-green; b) basic—rodamine B. 3. Relative tenacity of raw wool.



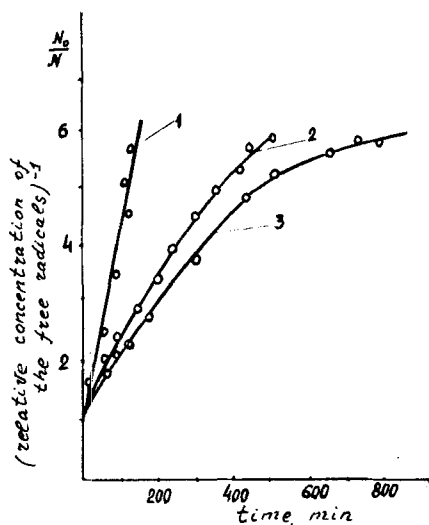
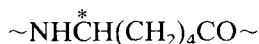


FIGURE 4 Loss kinetics of free radicals (vacuum irradiation at 298 K, Dose—8 Mrad) in: 1—polykapronamide; 2—natural silk; 3—wool.

centers' loss was intensified in the presence of air oxygen. While burning samples up to 298 K irradiated at 77 K various unstable forms of macroradicals were transferred into relatively stable form



### GENERATION KINETICS AND FREE-RADICAL CENTERS' LOSS IN DYES

Changes in the coloristic features are not observed when dyeing solutions are "softly" exposed to various types of peroxides and radiation doses are less than 15 Mrad.

But when they are exposed to "harder" oxidation or radiation effects there can be a decomposition of chromophore structure of the dyes. At the same time changes in dyes' dispersity takes place, as can be clearly confirmed by chromatographic means.

Free radical centers of such groups as  $\text{H}_2\text{N}$ -,  $\text{HN}$ <, alkyl  $\text{HO}$ -, as well as *N*-vicynal  $\text{CH}_2$ -groups in alkyl substitutes play an essential role in the generation on the dyes' particles, as evidenced by the results obtained by EPR-spectroscopy. The experimental data available indicate that only those dyes which have at least one of the above-mentioned groups can be fast-fixed in fibers.

Studies of the accumulation and the loss of the free radical centers in dyes show (Figure 5) that this process is well described for anthraquinonic dyes by the equation:

$$(C_0/C) - I = K \cdot \tau^\alpha$$

where

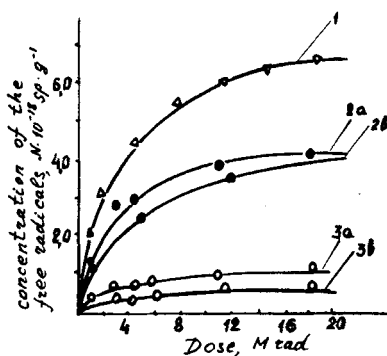


FIGURE 5 Dose relationship of free radicals' concentrations in dyed fibers and dyes (vacuum irradiation at 298 K; dye content in fiber—2.5–3.0 g·kg<sup>-1</sup>): 1—natural silk, dyed with acid methanyl yellow; 2—wool, dyed with a) Disperse blue R and b) acid methyl yellow; 3—dye a) acid methanyl yellow and b) disperse blue R.

$C_0$  and  $C$ —are initial and current concentrations of free radicals;

$K$  and  $\alpha$ —are factors, where the values of  $\alpha$  are in the range of 0.36–0.51, that is similar to Weir's equation specifying the reaction kinetics in the solid state.<sup>32</sup>

The value  $\Delta E_i = 150 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$ .

Chemical and radiation “activation” may result in the formation of semiquinone radicals in anthraquinonic dyes, and of nitroxyl centers in amino- and imino-groups of the dyes, including the localization of an uncoupled electron on *N*-vicynal C-atoms of alkyl substitutes. The recombination of dye particles containing free radical centers results in their aggregation and the formation of coarse, disperse particles. Their spectrophotometric features are similar to the original dye. Such particles are clearly determined by means of thin-layer chromatography and electron microscopy.

### SOME REGULARITIES OF DYES' FIXING IN FIBERS

The following are necessary requirements for achieving fixation of dyes in fibers when recombination addition reactions:

- the availability of polymer and dye functional groups suitable for the localization of the free radical centers;
- polymer transformation into the high elasticity state and introduction of the required quantity of dyes;
- chemical and radiation “activation” of the “polymer-dye” system and creation of the conditions suitable for the recombination processes in it.

Temperature increases of the fixing treatment from 333 up to 373 K increases the rates of the recombination addition reactions almost 10 times. The processes causing the dyes' fixing in the polymer substrates are diffusion controlled. The sorption dyes process takes place during the polymer substrate swelling. At the

same time macromolecule segmentary movement is considerably increased as is the migration power of the dye particles. Naturally, the transfer of unpaired electrons by the particles is facilitated. The kinetics of the accumulation and the loss of the free radicals in the "fiber-dye" system as a variant of a heterogeneous process can be described by Crank's simplified equation<sup>33</sup>:

$$\frac{N}{N_p} = \frac{4}{r} (D_\pi)^{0.5} \cdot \tau^{0.5}$$

where

$N$  and  $N_p$ —is a current and an equilibrium concentration of free radicals, respectively;

$D$ —a diffusion coefficient of a free radical center;

$r$ —radius of the swelled fiber.

It has been reported that "W-disperse dyes"<sup>18-20</sup> radiation-initiation system is of great interest. The disperse dyes' fixation in W can be carried out as a result of the recombination addition and of the enlargement of dye particles. The additional intramolecular "bridges" which appear during radiation treatment also favor the dyes' fixation in polymer substrates.

The results of the chromatographic analysis have shown that fractions correlation of non-ionogenic dyes' co-valence, bounded with keratin and aggregated under the radiation effect, is 4:1 for XIV dye and 7:3 for XX, respectively. The dyes' fixation in the radiation initiation of "PCA-disperse dyes" system appears to be of a different nature. The effect of anthracenic dye additives on the generation of the free radical centers in PCA is quite obvious (Table I).

However, semiquinone radicals of a different chemical nature do not essentially affect the loss kinetics of



macroradicals in the polymer substrate. In addition, PCA dyes' fixation is fast enough (Figure 6).

It should be noted that high resistance<sup>7,9,21,27</sup> to "washing," to "perspiration," to "wet" and "dry" rubbing has been achieved in all modes of fixing the dyes of

TABLE I

Content of  $\sim\text{NH}\overset{*}{\text{C}}\text{H}(\text{CH}_2)_4\text{CO}\sim$  microradicals in modified polykapronamide irradiated at 77 K.  
Dose is 14 Mrad

Modifying Agent —disperse dye	Index	Fraction
Alizarine	XII	0.50 ± 0.10
Violet R	XIV	0.47 ± 0.09
Blue R	XV	0.42 ± 0.08
Yellow 6 z	XVII	0.03 ± 0.02
—	—	0.02 ± 0.01

different classes used in the fiber material studied. Structural-mechanical features of fast-dyed fibers are similar to those dyed using conventional methods. The results of extraction treatment with acetone, DMF, pyridine: aqueous pyridine solutions including methods of hydrolysates thin-layer chromatography: extreme shifts on DTA, TGA and DSC curves: re-sedimentation of polymers and re-synthesis of azo-dyes prove the fixation of the dye particles in the polymer substrate.

Reaction relations in fiber vary due to the nature of the fiber-forming polymer and the "graft" compound:

1. Generation of free-radical centers in fiber-forming polymers;
2. Generation of free-radical centers in a dye molecule;
3. Re-combination of free-radical polymer forms and dyes with the subsequent formation of co-valent bonds;
4. Recombination of macromolecules' free-radical centers with the following formation of interchain "bridges" and mechanical "seizure" of dye particles;
5. Recombination of free-radical forms of dye molecules and the formation of huge dye aggregates, "squeezed" in structural elements of the polymer substrate and which form peculiar clathrates (complexes "inclusions");
6. Oxidative destruction of the chromophore part in dye molecules.

The last two groups are naturally undesirable and their role should be kept to a minimum. Process conditions determine the selectivity of the recombination addition reactions, thus, the ionogenic dyes' fixation in S, W and PCA occurs mainly in accordance with the third item; the disperse dyes' fixation takes place mostly according to the 4th and 5th items and in W and S according to the 3rd and 5th items.

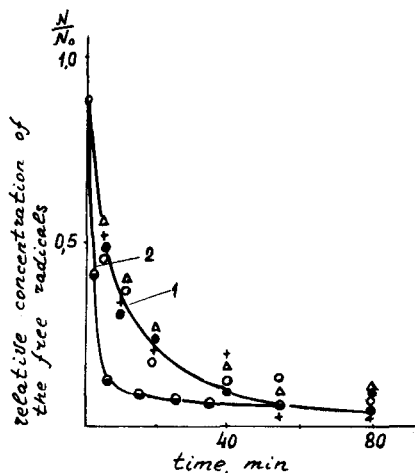


FIGURE 6 Loss kinetics of N-vicynalic macroradicals in polykapronamides at 348 K. 1—Experimental curve for the samples dyed with:  $\pm$ —alizarine;  $\Delta$ —disperse violet R;  $\circ$ —disperse yellow 6 z; and  $\bullet$ —excluding additives. 2—Theoretical curve obtained on the assumption of the recombination addition reaction,  $\bullet$ .

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