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The effect of reagent structure and the medium on radical pair recombination in polymers

Victor B. Ivanov, Elizabeth Yu. Khavina*

N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Street, 119991 Moscow, Russia

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ABSTRACT

Triarylcarbinols, the recombination products of ketyl and aminyl radicals identified by visible absorption spectra as relevant triarylmethane dyes, are formed during irradiation of poly(methyl methacrylate), poly(vinyl chloride), polystyrene and cellulose triacetate films containing substituted benzophenones and aromatic amines. Quantum yields of the reactions are determined. The features of reagents and polymer structures effect on the formation rates and yields of products are discussed. The reaction only proceeds in local zones of relatively large (~ nm) size, as is found based on the analysis of quantum yield dependence on amine concentration. This stipulates the presence of magnetic-spin effects leading to a significant (by 10–20%) product accumulation rate decrease in poly(vinyl chloride) and polystyrene as external magnetic field is applied. A mechanism of significant photochemical post-effect in films produced from chlorine-containing solvent is suggested and kinetic description is proposed. The formation of dye at irradiated film treatment by HCl is diffusion limited. This allows using the reactions studied in the investigations of both slow and fast diffusion processes in polymers.

1. Introduction

Short-living radical pairs are immediate predecessors of free radicals and are, therefore, of the prime importance for chemical transformation, modification and degradation of polymeric materials. Photochemical generation of radical pairs not merely expands experimental possibilities of investigation processes with participation of these extremely active particles, but also allows study of their transformation at low temperatures typical of common operation conditions of the articles. The majority of works in this field is devoted to analysis of radical pairs formed under the interaction of a photoinitiator (aromatic ketone) with additional reagent, phenol [1–4] or aromatic amine [4–6]. This is generally specified by the fact that in this case both the formation rate and radical pair yield increase, as well as additional possibilities for their control by typical phenoxy and aminyl radical spectra occur.

Scientifically, interest in studying radical pairs formed in reactions of low molecular reagents in solid polymers is associated with intention to determine the role of spin, molecular and chemical dynamics in processes of their evolution [4]. Also the attempts to develop investigation methods for local structure and molecular dynamics in solid polymers, polymeric glasses, especially, based on studies of the processes with radical pairs as kinetic probes are deemed to be prospective [3,4].

Realistically, interest in this problem is induced by the importance of understanding the mechanisms of antioxidants interaction with additives or chromophore polymer groups, because these processes may significantly determine operational performance of polymeric materials.

The main goal of this work is analysis of reagents and polymeric matrix structure effects on radical pair, formed by ketyl and aminyl radicals, recombination product yield. The subject of inquiry selection is generally intended by simplicity and unambiguousness of determination of particularly recombination products (triarylcarbinols) based on spectrophotometric analysis of triarylmethane dyes, formed by effecting irradiated samples by strong acids [6].

2. Experimental

Aromatic ketones, benzophenone and its *p*-substituted analogues (4,4′-dimethyl-, 4,4′-dichloro-, 4-bromo-, 4-hydroxy-, 4-methoxy- and 4,4′-dimethylaminobenzophenone), as well as diphenylamine of reagent grade were purified by double re-crystallization from ethanol. Phenyl-β-naphthylamine was detached from impurities by consecutive chromatography on charcoal and aluminum oxide. 6-Ethoxy- and 8-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, 4,4′-di-*tert*-butyl- and 4,4′-dimethoxydiphenylamine were synthesized in IOC RAS [7] and ICP RAS, respectively.

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* Corresponding author. Tel.: +7 495 939 73 14; fax: +7 495 939 74 83.
E-mail address: kelizabeth@ya.ru (E.Yu. Khavina).

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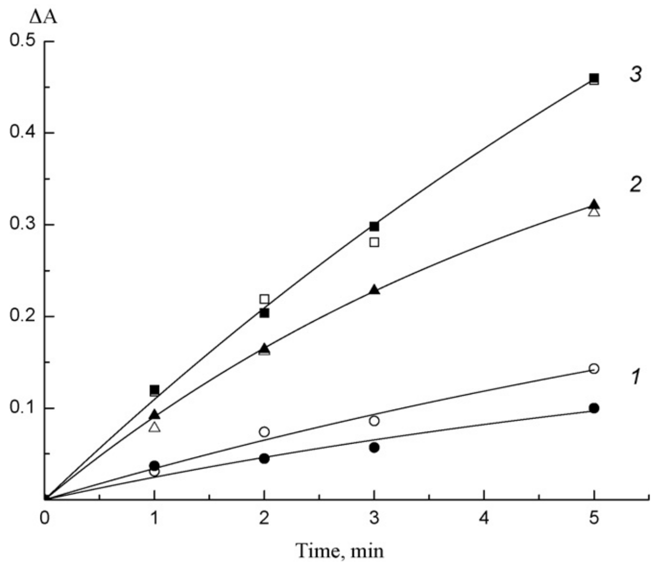

Fig. 1. The effect of ketone nature on the dye yield at irradiation of PMMA films containing diphenylamine (0.4 mol/kg) and ketone (0.1 mol/kg) in air by light with λ = 365 nm; ketone: *1* – 4,4′-dimethylaminobenzophenone, *2* – 4,4′-dimethylbenzophenone, *3* – 4,4′-dichlorobenzophenone. Time of further treatment in HCl vapors: 48 (△, □) or 168 (▲, ■) hours (25 (○) and 50 (●) hours for 4,4′-dimethylaminobenzophenone).

Commercial polymers: polystyrene (PS) PSM-115 with molecular mass (*M*) ~ 300,000, poly(vinyl chloride) (PVC) M-64 with *M* ~ 65,000 and poly(methyl methacrylate) (PMMA) Plexiglas 8N with *M* ~ 160,000, were used without additional purification. Cellulose triacetate (CTA) with *M* ~ 330,000 and acetylation degree 62.5% was purified by precipitation by ethanol from glacial acetic acid solution and further extraction by ethanol.

Films 200 μm thick were formed by slow evaporation of the solvent (methylene chloride for PS, PMMA and CTA, and 1,2-dichloroethane for PVC) from 5% polymer solution. Necessary additives (ketones and aromatic amines) were introduced into the polymer solution immediately prior to film preparation.

The samples were irradiated in air or in vacuum by light with λ = 365 or 405 nm separated from total spectrum of high pressure Hg-lamp DRSH-1000 using optical filters BS6 and UFC6 (365 nm) or ZhS10 (405 nm). Incident light intensity was measured using thermocell AT-50 and chemical actinometer based on benzophenone phototransformation proceeding in the absence of additional reagents in PVC with quantum yield equal 0.16 [8].

To reach complete transformation of triarylcarbinol into relevant triarylmethane dye, after irradiation films were exposed to HCl vapors or dissolved in chloroform added by concentrated hydrochloric acid. Product yields determined by these two techniques coincide within the experiment accuracy (≤10%). The absorption spectrum of reaction product of benzophenone with diphenylamine in polymers ($\lambda_{max} = 502$ nm) is in agreement with the 4-phenylaminophenyldiphenylcarbonium ion spectrum in nonpolar solvents. Taking into account this circumstance, the extinction coefficient of the ion in chloroform (3.65×10^4 dm^3/(mol cm) [9]) was used for the determination of this product concentrations. The same extinction coefficient can be employed for yield estimations of dyes produced in course of interaction of benzophenone derivatives with diphenylamine. As a background of this conclusion can be considered the well-known data that the extinction coefficients in the sequence of triarylmethyl cations containing Cl, CH_3 or OCH_3 groups in *p*-position are distinguished less than 5% [10]. As a complementary argument can be used the fact that even the introduction of the dimethylamino group, a strong electron-donor substituent, causes the change in extinction coefficient of 4-phenylaminophenyldiphenylcarbonium ion not more than 12% [9]. The extinction coefficient 1.08×10^5 dm^3/(mol cm) was used for the dyes produced during interaction of 4,4′-dimethylaminobenzophenone with diphenylamine or phenyl-β-naphthylamine by analogy with Malachite Green [11] and its derivatives having additional substituents in *p*-position of the phenyl ring [12]. The value equal 3.65×10^4 dm^3/(mol cm) was assumed for the dye formed in the reaction of benzophenone with 8-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline guided by similarity with the 4-dimethylaminophenyldiphenylcarbonium ion spectrum [9].

The spectra of phosphorescence were recorded on a unit consisting of a light source (a DKSSh-150 Xe lamp), an SPM-2 excitation monochromator, a thermostatically controlled cuvette section, a recording MC-80 monochromator, and a recording system (an FEU-128 photomultiplier and a K-2-1 automatic recorder). The film samples in special holders were placed at an angle of 45° to the incident light beam. The excitation wavelength was 365 nm, and the recording wavelength, 420 nm.

Absorption spectra in UV and visible ranges were recorded by spectrophotometers Specord UV–Vis and MultiSpec-1501.

Absorption spectra as well as formation and death kinetics of intermediate products were recorded on a device of nano-second laser photolysis [1,13]. For the excitation source, a nitrogen laser PRA LN 1000 (with the pulse length 1 ns, λ = 337 nm, and repetition frequency 10 Hz) was used. Kinetic curves (by 16–128 laser pulses) were accumulated and averaged-out using a high-speed analog-to-digital converter (flash encoder) UF.258.

3. Results and discussion

It is found that irradiation of PMMA films containing benzophenone derivatives with various substituents in the *p*-position ($-CH_3$, $-OCH_3$, –OH, –Cl, –Br or $-N(CH_3)_2$-groups), together with diphenylamine, by light with λ = 365 nm, leads to formation of triarylcarbinols identified by typical absorption of appropriate triarylmethane dyes after irradiated films treatment by HCl.

Taking into account data from the literature [5,6,14] and a circumstance that the absorption spectrum of dyed product derived from benzophenone and diphenylamine is fully coincident to the absorption spectrum of 4-phenylaminophenyldiphenylcarbonium ion ($PhNHC_6H_4C^+Ph_2$) [9], $PhNHC_6H_4C^+(C_6H_4R)(C_6H_4R')$ dye formation from $^1[RC_6H_4C^{\bullet}(OH)C_6H_4R' \ldots PhN^{\bullet}Ph]$ radical pair can be presented as a sequence of the following basic reactions (Scheme 1):where $PhNHC_6H_4C(OH)(C_6H_4R)(C_6H_4R')$ is triarylcarbinol, R and/or R′ = H, CH_3, Cl, Br, OH, OCH_3 or $N(CH_3)_2$.

$$^1[RC_6H_4C^{\cdot}(OH)C_6H_4R' \ldots PhN^{\cdot}Ph] \rightarrow PhNHC_6H_4C(OH)(C_6H_4R)(C_6H_4R')$$

$$PhNHC_6H_4C(OH)(C_6H_4R)(C_6H_4R') + H^+ \rightarrow PhNHC_6H_4C^+(C_6H_4R)(C_6H_4R') + H_2O,$$

Scheme 1.

Table 1
Quantum yields of the dye formation in PMMA films, containing diphenylamine (0.4 mol/kg) and various ketones (0.1 mol/kg).

Ketone	Relative rate, min^{-1}	Absorbance at 365 nm	Quantum yield, mol/Einstein
Benzophenone	0.062	0.13	0.022
4-Bromobenzophenone	0.073	0.18	0.020
4,4′-Dichlorobenzophenone	0.102	0.19	0.026
4,4′-Dimethylbenzophenone	0.079	0.17	0.022
4-Hydroxybenzophenone	0.068	0.18	0.018
4-Methoxybenzophenone	0.054	0.17	0.015
4,4′-Dimethylaminobenzophenone	0.021	$\gg 1$	0.002

Table 2
Quantum yields of the dye formation in PMMA films, containing ketone (0.1 mol/kg) and various amines (0.4 mol/kg).

Ketone	Amine	Quantum yield, mol/Einstein
Benzophenone	Diphenylamine	0.022
Benzophenone	6-Ethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline	≤ 0.0007
Benzophenone	8-Methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline	0.013
Benzophenone	4,4′-Di-*tert*-butyldiphenylamine	≤ 0.0008
Benzophenone	4,4′-Dimethoxydiphenylamine	≤ 0.002[a]
4,4′-Dimethylaminobenzophenone	Diphenylamine	0.002
4,4′-Dimethylaminobenzophenone	Phenyl-β-naphthylamine	≈ 0.001

[a] There are no pronounced maxima in absorption spectra after exposition in HCl vapors and the samples have yellow-green color. This is the evidence, that the dominating process is the formation of dimethoxydiphenylamine oxidation products. Hence this value is the maximum estimation of the recombination product yield. Actually the quantum yield is significantly lower. The possible formation of the recombination products is bound up probably with admixtures of diphenylamines that do not contain substituents in both *p*-positions.

Table 3
Stationary concentrations and quantum yields of the dye in various polymers, containing benzophenone (0.1 mol/kg) and diphenylamine (0.4 mol/kg).

Polymer	Stationary concentration, mmol/kg	Quantum yield, mol/Einstein
Polystyrene	2.1	0.0046
Poly(vinyl chloride)	1.4	0.0062
Poly(methyl methacrylate)	3.3	0.022
Cellulose triacetate	5.3	0.029

The process rate essentially depends on the substituent nature (Fig. 1) which in many cases is stipulated by increasing absorption at the irradiation wavelength due to ketone spectrum displacement to the long-wave region (Table 1). For example, the reaction rate of 4,4′-dichlorobenzophenone and 4,4′-dimethylbenzophenone is 1.6 and 1.3 times, correspondingly, as many as of non-substituted benzophenone. The effect of substituents on quantum yields of the reaction is much less expressible. Quantum yields for 4,4′-dimethylbenzophenone and benzophenone are practically equal, and for 4,4′-dichlorobenzophenone is distinguished only in 30%. The exclusion is 4-methoxybenzophenone, for which the quantum yield decrease compared with non-substituted ketone is about 30%, and 4,4′-dimethylaminobenzophenone (Michler's ketone) have by an order of magnitude lower reactivity. These results correlate well with the literary data witnessing about reactivity decrease for benzophenone derivatives with strong electron-donor substituents in radical polymerization initiation processes in systems, which include amines as co-reagents [15]. The effects observed witness that in polymeric matrix the initial stage is also the electron transfer, followed by slower stage of the proton transfer. Strong electron-donor substituents significantly decrease affinity to electron that leads to a reduction of the radical pairs yield and, as a consequence, the recombination products yield.

More detailed analysis of the data from Table 1 allows two more important additional conclusions:

- introduction of rather voluminous substituents (CH_3-groups) into *p*-position, and substituents which change noticeably molecular mass of the reagent (Cl atoms) does not decrease the quantum yield of the recombination product, and in the case of Cl atoms it even increases the quantum yield;
- heavy atoms (Br), which abruptly decrease the lifetime of radical pairs in micellar solutions due to acceleration of intersystem crossing [13], just insignificantly (less than by 10%) decrease the reaction quantum yield in PMMA.

Note that the absence of heavy atom effect confirms the previous conclusion [4] that the spin dynamics is not the limiting factor for radical pair recombination in solid PMMA.

Variation of aromatic amine structure leads to a significantly larger scale change of the reaction quantum yield (Table 2). As follows from the data obtained, the quantum yield of triarylcarbinol formation at benzophenone interaction with 8-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline is just by 40% lower than at benzophenone interaction with dimethylamine in the same concentration, whereas virtually, the reaction with 6-ethoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline does not proceed (the quantum yield is below 7×10^{-4}). This is the additional evidence that similar to micellar systems, recombination in polymers is performed via ketyl radical attack of aminyl radical in the *p*-position. In full accordance with this conclusion, diphenylamine derivatives having substituents in the *p*-position either do not enter the reaction at all (4,4′-di-*tert*-butyldiphenylamine, quantum yield below 8×10^{-4}) or give dyed products with insignificantly low yield (4,4′-dimethoxydiphenylamine, quantum yield below 2×10^{-3}). Although substitution of one phenyl ring by naphthyl one leads to a significant decrease of the quantum yield (Table 2), nevertheless it is not crucial obstacle for the reaction performance even with such an inactive compound, which 4,4′-dimethylaminobenzophenone is.

The polymer structure has a noticeable effect on the yield of radical pair recombination product (Fig. 2). As is seen from Fig. 2, rates of dye accumulation during benzophenone and diphenylamine interaction in PMMA and CTA (without additional acid treatment) in 15 and 6.6 times, correspondingly, lower than in PVC. After HCl treatment of irradiated polymer samples, when all the 4-phenylaminophenyldiphenylcarbinol formed previously converts into corresponding dye, the correlation between rates (and quantum yields) of dye accumulation changes both quantitatively and qualitatively (Table 3). In the sequence PS–PVC–PMMA–CTA, the quantum yield of benzophenone reaction with diphenylamine increases by more than 6 times. It may be suggested that in the

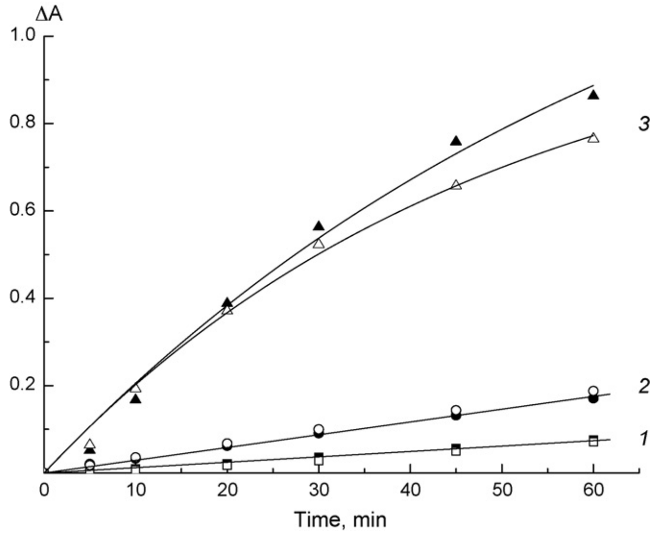

Fig. 2. The effect of polymeric matrix on the dye yield at irradiation of films containing diphenylamine (0.4 mol/kg) and benzophenone (0.1 mol/kg): *1* – PMMA, *2* – CTA, *3* – PVC. Irradiation in the field of permanent magnet having B = 0.18 T (△, □, ○) or in the absence of additional magnetic field (▲, ■, ●) without additional treatment in HCl vapors.

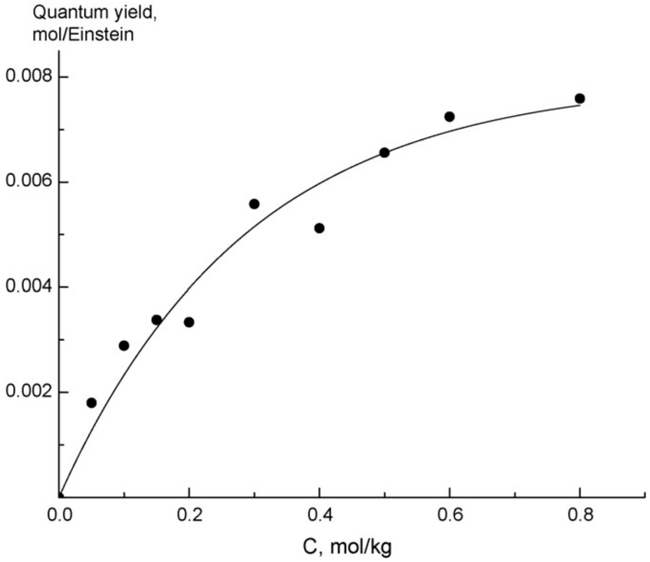

Fig. 3. The quantum yield dependence of triarylmethane dye formation on diphenylamine concentration in PS at irradiation of samples containing 0.1 mol/kg benzophenone by light with λ = 365 nm in air. After irradiation of films, they were exposed to HCl vapors in darkness for 72 h. Points show experimental data and continuous curve – calculation by Eq. (1).

sequence PVC–PMMA–CTA, the quantum yield increase relates to increasing role of small-scale molecular dynamics associated with the presence of rather large sized side ester groups in PMMA and CTA. In the case of CTA, the apparent additional factor is the structure porosity due to large size of macromolecule unit. At such approach to analysis of the experimental results, PS also having voluminous side groups is of exceptional position. The reasons for that become clear, when we account for that stationary concentration of the recombination product, detected after a long-term (≥1 h) irradiation of the films, is significantly (by 1.5 times) higher in PS than in PVC, although the quantum yield in PS is lower by the same degree (1.4 times) (Table 3). High steady-state concentration of the product testifies that PS has many local areas (cites), where the free volume and/or molecular mobility are sufficient for regrouping of ketyl and aminyl radicals forming a radical pair, which provides for recombination proceeding with triarylcarbinol formation. At the level of quantum yields, possibilities for reaction proceeding, related to a local dynamics, are not realized in PS because of lower radical pair yield. In turn, this is stipulated by quenching of benzophenone triplet state by phenyl rings with reversible formation of a biradical adduct [16]. This suggestion is substantiated by data obtained using the laser photolysis technique, that the rate of benzophenone triplet state deactivation in PS is much higher than in PVC, PMMA and CTA, which also include diphenylamine additives.

The dependence of recombination quantum yield φ or reaction rate w on diphenylamine concentration in PS and in PMMA is properly described by an equation analogous to modified Perrin equation (1), that takes into account the dependence of relative concentration of ketone/amine pairs (preliminary products, which are able to interact with triarylcarbinol formation) on amine concentration (Figs. 3 and 4, curve *2*):

$$\frac{\varphi}{\varphi_{\infty}} = \frac{w}{w_{\infty}} = 1 - \exp(-NV_r c_A) \qquad (1)$$

where φ_{∞} and w_{∞} are quantum yield and the reaction rate at the limiting ("infinitely large") diphenylamine concentration; c_A is diphenylamine concentration; $V_r = 4/3\pi R_r^3$ is the volume of cage with radius R_r, where reaction proceeds, and N is the Avogadro number.

The radius of benzophenone interaction with diphenylamine, R_r, in PS and PMMA with triarylcarbinol formation, calculated by data in Figs. 3 and 4, curve *2*, are ~1.1 and 1.4 nm, respectively. The values obtained are significantly greater than the sum of molecular radii of the reagents. This confirms the above conclusion that the reaction proceeds exclusively in local areas of relatively big size, which areas may be considered as peculiar nanoreactors.

According to the proposed mechanism (Scheme 1), triarylcarbinol represents a product of heminal recombination of radical pair consisting of ketyl and aminyl radicals and hence the primary interaction of ketone and amine with formation of radical pair is one of key factors of the process. The data on the quenching of phosphorescence of benzophenone by diphenylamine in PMMA (Fig. 4, curve *1*), as well as the results of studying samples by laser pulse photolysis indicate that, at sufficiently high concentrations of amine ($c_A \geq 0.4$ mol/kg), almost all triplet states of benzophenone

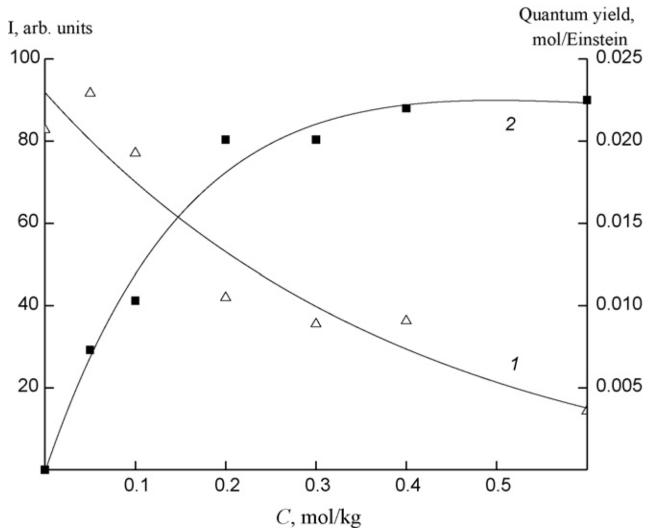

Fig. 4. Relative intensity of phosphorescence of benzophenone (0.1 mol/kg) (*1*) and the quantum yield of dye formation (*2*) as a function of concentration of diphenylamine in PMMA. T = 20 ± 1 °C, in vacuum, and an excitation wavelength of 365 nm. The points correspond to the experimental data, and the curves are related to the calculations by Eqs. (2) and (1), respectively.

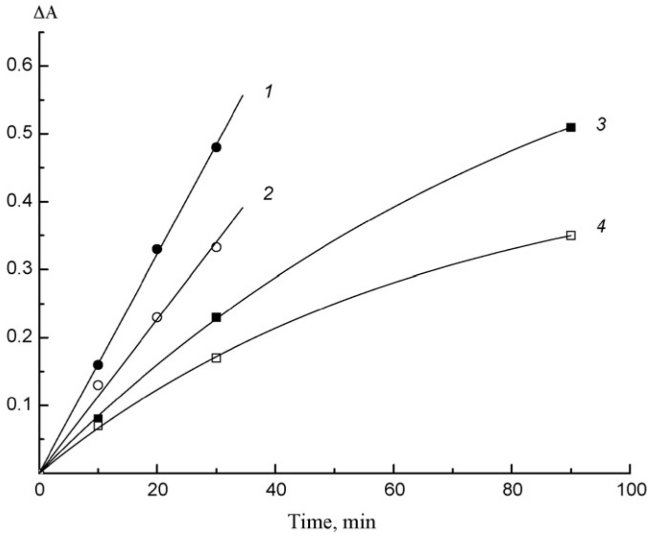

Fig. 5. The effect of magnetic field on the dye yield in PS at irradiation of films containing benzophenone (0.1 mol/kg) and diphenylamine, 0.3 mol/kg (curves *1* and *2*) or 0.1 mol/kg (curves *3* and *4*). Curves *2* and *4* are measured at application of external magnetic field with $B = 0.18$ T and curves *1* and *3* – without magnetic field (in the Earth magnetic field with $B = 0.05$ mT).

formed under illumination interact with diphenylamine, giving radical pairs. The phosphorescence quenching is described satisfactorily by the Perrin equation (2) [17],

$$I = I_0 \exp(-NV_q c_A)] \qquad (2)$$

where I and I_0 are intensities of phosphorescence of benzophenone in the presence and absence of quencher diphenylamine, $V_q = 4/3\pi R_q^3$ is volume of the quenching sphere with radius R_q.

The value of the radius of interaction R_q in PMMA calculated from the experimental data (Fig. 4, curve *1*) is approximately 1.0 nm. This quantity is close to the values of molecular radii and is typical of the exchange interaction between the donor and quencher, when the quenching occurs by the mechanism of energy transfer (for triplet states), electron transfer, or hydrogen transfer (both for triplet and singlet states). Therefore, the primary interaction of ketone and amine is described by a simple statistical model disregarding, particularly, the well-known concepts on complex formation between molecules of ketone and amine [18].

Radius R_r of interaction of ketone and amine with the formation of triarylcarbinol determined in PMMA by Eq. (1) is around 1.4 nm, which is significantly higher that the R_q value for the phosphorescence quenching described by expression (2). By this is meant that the reaction occurs in large cages only, where the free volume is sufficiently large not only for a considerable change in the hybridization of reacting centers, but for the rearrangement of particles necessary for changing their mutual positions.

The presence of local cites of a significant size (~ nm) in polymeric glasses, where recombination proceeds, is, apparently, the basic condition for manifestation of substantial magnetic effects observed in PVC (Fig. 2) and PS (Fig. 5). In accordance with the theory [13], imposition of the external magnetic field which reduces the rate of triplet–singlet conversion of the main part of radical pairs present in the nanoreactors leads to a decrease of recombination product yield (Fig. 5, comp. curves *1* and *3* in the absence of field with analogous curves *2* and *4* for the reaction proceeding in constant magnetic field) (Scheme 2):where $^{3}\mathrm{PhC({=}O)Ph}$ is the triplet state of ketone (benzophenone) molecule; $^{3}[\mathrm{PhC^{\bullet}(OH)Ph\ldots PhN^{\bullet}Ph}]$ and $^{1}[\mathrm{PhC^{\bullet}(OH)Ph\ldots PhN^{\bullet}Ph}]$ are triplet and singlet state of the radical pair, respectively.

$$\begin{array}{lcl}
{}^{3}\mathrm{PhC({=}O)Ph} + \mathrm{PhNHPh} & \rightarrow & {}^{3}[\mathrm{PhC^{\cdot}(OH)Ph\ldots PhN^{\cdot}Ph}] \\
{}^{3}[\mathrm{PhC^{\cdot}(OH)Ph\ldots PhN^{\cdot}Ph}] & \rightarrow & {}^{1}[\mathrm{PhC^{\cdot}(OH)Ph\ldots PhN^{\cdot}Ph}] \\
{}^{1}[\mathrm{PhC^{\cdot}(OH)Ph\ldots PhN^{\cdot}Ph}] & \rightarrow & \mathrm{PhNHC_6H_4C(OH)Ph_2} \\
{}^{1}[\mathrm{PhC^{\cdot}(OH)Ph\ldots PhN^{\cdot}Ph}] & \rightarrow & \mathrm{PhC({=}O)Ph} + \mathrm{PhNHPh}
\end{array}$$

Scheme 2.

Note that since the overwhelming majority of radical pairs is formed in small size zones of molecular diameter value and represents contact radical pairs, processes of their evolution are not limited by spin dynamics, and the main direction of their transformation is disproportioning with primary reagent regeneration [4]. This is the reason that total death rate of radical pairs detected by means of the laser photolysis does not change at imposition of the external magnetic field.

Dye formation directly during irradiation (Figs. 2 and 6) and the presence of high and durable photochemical post-effects (Fig. 6, sections of kinetic curves after the moment, when irradiation stopped, marked with arrows) is the important feature of the process proceeding in chlorine-containing polymers (PVC) and in PMMA and CTA films prepared by using chlorine-containing solvent ($\mathrm{CH_2Cl_2}$). In PVC, already at irradiation of samples, the dye yield is so high that further treatment of films or solutions with an acid does not cause a noticeable increase of dyeing. In PMMA and CTA, irradiation produces relatively low amount of dye and film dyeing is sharply intensified in case of HCl vapor treatment. This effect is most intensive for CTA. Dye accumulation during irradiation of the films produced from chlorine-containing solvent proceeds with clearly expressed induction periods (Fig. 6, compare points at $t \leq 10$ min and $10 < t < 30$ min) and the maximum rate is so higher, the higher the formation and recombination rate for radical pairs is (compare curves *1* and *2* for benzophenone and 4,4′-dimethylbenzophenone reactions with diphenylamine in PMMA). This testifies that dyeing both directly at irradiation and in dark period relates to interaction between triarylcarbinols and HCl formed as a result of induced degradation of chlorine-containing solvent residues present in the sample. Such processes are well-known [19] and represent one of the key stages of photoinitiator synergism in the triple system which includes an aromatic ketone,

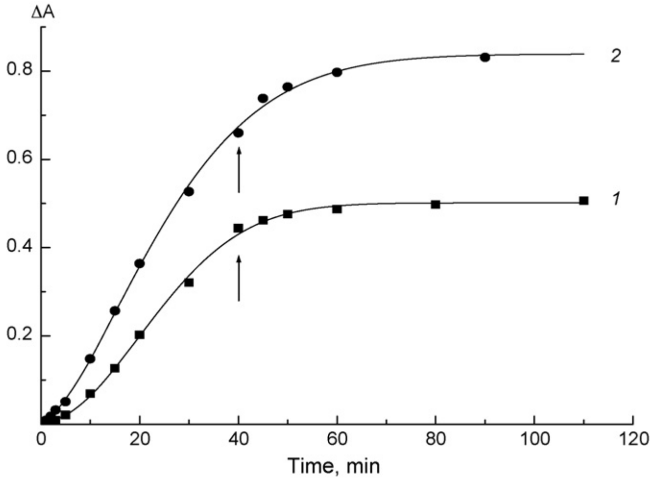

Fig. 6. Kinetic features of triarylmethane dye formation induced by significant photochemical post-effect at irradiation of PMMA films containing 0.1 mol/kg benzophenone (*1*) or 4,4′-dimethylbenzophenone (*2*) and diphenylamine (0.4 mol/kg) in air by light with $\lambda = 365$ nm (total irradiation time is 40 min) and further exposure to darkness. Points show experimental data and continuous curves – calculation by Eqs. (3) (initial parts of photochemical stage) and (4) (dark stages).

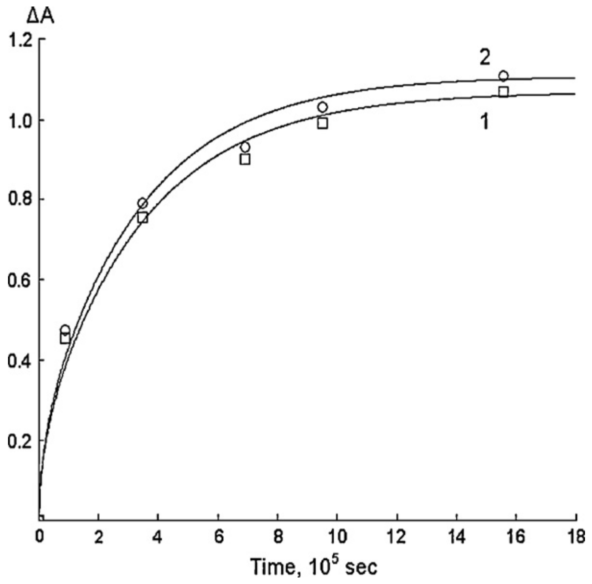

Fig. 7. Kinetic curve of dye accumulation at irradiated PMMA films exposure to hydrochloric acid vapors. The samples containing benzophenone (0.1 mol/kg) and diphenylamine (0.4 mol/kg) were prior irradiated in air by light with λ = 365 nm during 60 min in permanent magnet field with B = 0.18 T (□) and in the absence of external magnetic field (○). Points show experimental data and continuous curves – calculation by Eq. (5).

amine and haloid-containing compound [20]. In accordance with these ideas, at relatively low transformation degrees, the dye accumulation kinetics at irradiation should be described by Eq. (3) which makes allowance for proceeding of two consecutive first order reactions: photochemical formation of triarylcarbinol and its further conversion to a dye by interaction with HCl:

$$c_d = c_{BA}\left\{1-\left[\frac{k_d}{k_d-k_c}\right]\exp(-k_c t)+\left[\frac{k_c}{k_d-k_c}\right]\exp(-k_d t)\right\} \qquad (3)$$

where k_c and $k_d = k_d^0 c_c$ are effective rate constants of triarylcarbinol formation and transformation to a dye; c_d is the dye concentration at the given moment of time, t; $c_{BA} = const$ is the concentration of "preliminary associates" (ketone and amine clusters) which transformation may cause formation of triarylcarbinol or a dye.

In the dark period, immediately after irradiation stop, the dye continues accumulating in accordance with the first order reaction Eq. (4):

$$\Delta c_d = [\mathrm{HCl}][1-\exp(-k_d t)] \qquad (4)$$

where Δc_d is concentration of the dye formed at the stage of photochemical post-effect by time moment t after irradiation stop; [HCl] is hydrogen chloride concentration in the film at the moment of irradiation stop.

As shown in Fig. 6, the experimental data obtained at the study of dyes accumulation in PMMA films containing benzophenone and 4,4′-dimethylbenzophenone, are described well by Eqs. (3) (photochemical stage, $t \le 40$ min) and (4) (dark stage (post-effect), $t \ge 40$ min) that confirm the above conclusions about the film dyeing nature directly at the stage of irradiation and the mechanism of extremely high photochemical post-effect.

On the background of the basic reaction of recombination of the primary radical pair to give the new product – triarylcarbinol – analyzed in this work, the reaction of photodegradation of the polymer (for example PMMA) is a side process. Upon irradiation of films prepared from CH_2Cl_2, the spectra display characteristic signals due to end radicals of PMMA, which are very stable under vacuum [19]. The kinetics of accumulation of radicals has a complex character: after a relatively small jump in accumulation at the initial instant of irradiation, a long stationary stage is observed, where the radicals are formed at an almost constant rate. The rate of accumulation of macroradicals increases with concentration of amine. The latter feature can be due to the synergistic type of the triple system under consideration, since, as was noted above, the film contains a residual solvent that cannot be removed under conventional conditions and participates in the process. Note that the results, which are indicative of the presence of radical reactions involving polymer and chlorinated solvent, offer additional verification of this mechanism, explaining the extremely high photochemical post-effects found in this work.

As shown above (see Fig. 1), to reach the maximum level of dyeing the films should be exposed to HCl vapors for rather long time (tens and hundreds of hours). Obviously, this is irrelevant to a low rate of triarylcarbinol interaction with HCl in the polymeric matrix, because typical reaction time for photochemical post-effect, when HCl is formed directly in the film, is not in excess of 10 min. It may be suggested, therefore, that rather low rate of the dye formation at irradiated film treatment by HCl vapors is stipulated by low diffusion rate of this reagent in PMMA films. More detailed analysis of dyeing kinetics confirms this suggestion.

In accordance with the theory, for a plate $2l$ thick, sorption of a substance from the environment with constant concentration is described by expression (5) [21]:

$$\frac{M_t}{M_\infty} = \frac{A_t}{A_\infty} = 1-\sum_{n=0}^{\infty}\left\{\frac{8}{(2n+1)^2\pi^2}\right\}\exp\left\{-\frac{D[(2n+1)^2\pi^2 t]}{4l^2}\right\} \qquad (5)$$

where M_t and M_∞ is total amount of diffusing substance entering the plate during time t and during unlimited time; A_t and A_∞ is absorbance of films due to dye formation during time t and during unlimited time; D is the diffusion coefficient.

As shown in Fig. 7, experimental data on kinetics of dye accumulation at HCl vapor treatment of preliminary irradiated films is described quite well by Eq. (5). The diffusion coefficient of HCl in PMMA determined from the data in Fig. 7 in accordance with Eq. (5), equals $1.2 \times 10^{-14}\ \mathrm{m^2/s}$. The value obtained conforms to the literary data for other hydrophobic polymers: PE, PET and polycaproamide ($D = 8 \times 10^{-11}$, 8×10^{-12} (an evaluation) and $2.5 \times 10^{-13}\ \mathrm{m^2/s}$, respectively [22]). This opens up new opportunities for the study of diffusion in polymers. The use of photochemical reactions, both considered in this work and others seems to be of particular prospect for studying quick mass transfer processes with application of pulse photoexcitation methods.

4. Conclusion

Thus, radical pair recombination in polymeric matrices with triarylcarbinols formation represents a general phenomenon and is typical for numbers of pairs formed with participation of some benzophenone and aromatic amines derivatives in polymers of various structures.

The critical behavior of recombination product yield dependence on the presence of substituents in the p-position to amino group testifies that both in polymers and micellar solutions the reaction proceeds in the p-position of aminyl radical.

Substituents in the p-position of benzophenone derivatives have a weak effect on the quantum yield of the process. This is, apparently, stipulated by the features of the present reaction mechanism, performed with participation of central C-atom of ketyl radical. The exception is strong electron-donor substituents which substantially reduce the electron affinity of ketones.

Sufficient range of recombination quantum yield change in the polymeric glasses studied (by 6 times) witnesses about high sensitivity of this process to the structure and molecular dynamics of the local environment. This opens up broad prospects for the use of radical pair recombination as a kinetic probe for studies of polymers.

Spin dynamics is not the limiting factor for evolution of radical pairs, however, in some polymeric systems (PVC and PS) it may, to some extent, affect the rate and direction of the process.

Only a small part of photoinitiators (0.5–5% appr. at large concentrations of the co-reagent, aromatic amine) exists in relatively large sized cites ($\geq$1 nm), where recombination of radical pairs is possible. The main part of them forms contact radical pairs, in which disproportionation dominates. For these radical pairs in all studied systems, magnetic-spin effects are absent.

The possibility of triarylcarbinols pulse generation using laser radiation allows application of these processes for the study of strong acids quick diffusion in polymeric systems.

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