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Branched Poly(methyl methacrylates) Modified by C_{60} Fullerenes

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Abstract—The poly(methyl methacrylates) of branched structure with a covalently bonded fullerene were synthesized by three-dimensional radical polymerization of methyl methacrylate with triethylene glycol dimethacrylate or allyl methacrylate in toluene containing C_{60}. The kinetics of copolymerization of methyl methacrylate with multifunctional co-monomers in the absence of fullerene is compared with that in its presence. The physicochemical characteristics and thermal stability of the obtained copolymers are also compared. The electron spin resonance (ESR) method was applied to study the kinetics of accumulation of the fullerene radicals in the course of the (co)polymerization of methyl methacrylate.

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The radical copolymerization of vinyl(idene) monomers with multifunctional monomers, in particular, with the dimethacrylates, in the mode of chain transfer, is a highly efficient one-step method for the synthesis of branched copolymers [1]. The macromolecule size and topological structure, including the length of the primary and cross-site chains and the number of terminal chains, can be varied easily by changing the ratio of the reactants [monomer : multifunctional co-monomer (branching agent) : chain transfer agent], the structure of branching and chain transfer (conventional or catalytic) agents, and the synthesis conditions (initiator concentration, temperature, and dilution).

Branched copolymers of methyl methacrylate (**I**) with dimethacrylate **II** are characterized by high solubility in various organic media, have low viscosity in solution [2], are able to absorb low molecular weight chemicals, such as water-soluble dyes [3], and serve as the polymeric containers of the latter. A useful set of properties of branched poly(methyl methacrylates) can be significantly enhanced for various practical purposes by modification with the low molecular weight compounds.

To modify the polymers fullerene C_{60} is often used [4–7]. This choice is certainly determined by its electrical, magnetic and optical properties [4, 5], as well as the biological activity [6]. The inclusion of fullerene in the polymer chain leads to a change in the properties of the latter, for example, increases its solubility in various media, including water [5]. Therewith the size and shape of the polymer coil, as well as optical and dielectric properties of macromolecules are changed [7].

The focus of the research are both guest–host fullerene–polymer supramolecular complexes obtained by the slow evaporation of solvent from the mixed solution [8], and the polymers with covalently bound fullerene [4]. The latter are produced usually by the multistage and complex reactions of the fullerene or its derivatives with polymers. However, due to the activity of the fullerene in the radical reactions, the polymers with covalently bound fullerene can be obtained also by a single-stage method through the radical polymerization of monomers bearing C=C bonds in a solution containing C_{60} [4]. Fullerene due to its double bonds is involved in the radical polymerization and becomes covalently bound to the polymer chains.

In the synthesis of fullerene-containing copolymers of branched structure the choice of a branching agent is extremely important, not only in terms of formation of molecular and topological structure, but also for controlling the number of the polymer chains additions to the fullerene core. In this respect allyl methacrylate

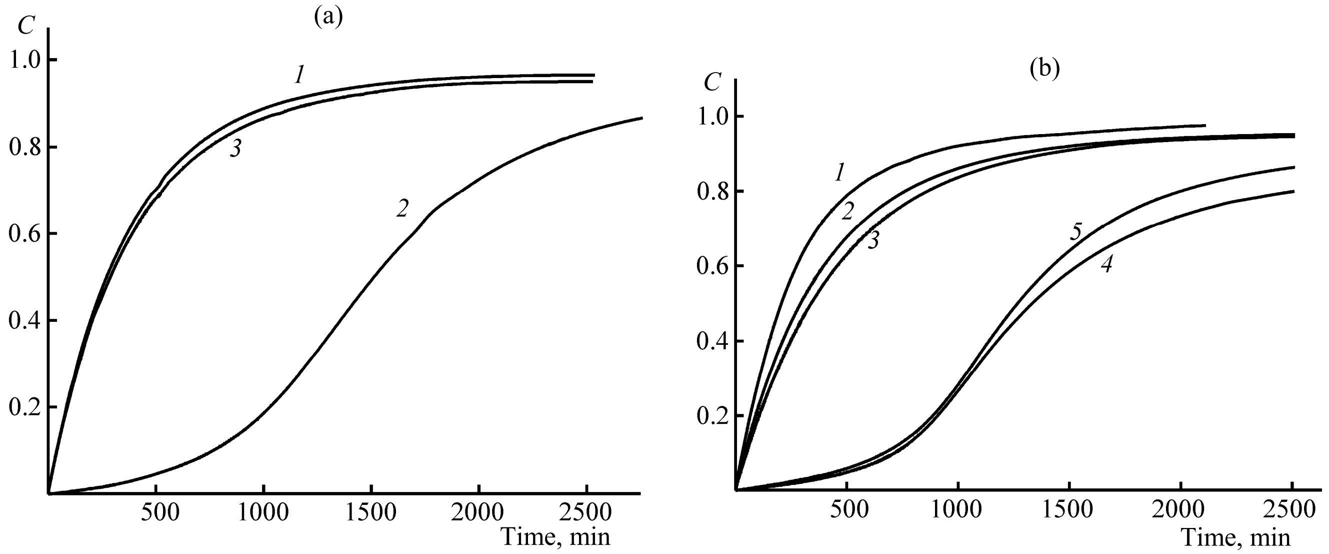

Fig. 1. (a*)* Kinetic curves of polymerization of monomer **I** in toluene in the absence (*1*) and in the presence of 0.78×10^{-3} M of fullerene (*2*) or cyanoisopropylfullerene (*3*) in the conversion *C*–time *t* coordinates; (b) Kinetic curves of copolymerization of monomer **I** with monomers **II** (*1*, *5*) and **III** (*2*–*4*) in the absence (*1*–*3*) and in the presence of fullerene (*4, 5*) or 1-decanethiol (*2*–*5*). The molar ratio [monomer **I**]:[monomer **II**, **III**]:[1-decanethiol] is 100:5:0 or 100:5:5, [Initiator] = 2×10^{-2} M, [Toluene] = 80 wt %, $T = 60$°C.

III is very interesting. Like methyl methacrylate, it is an electron-acceptor, and its double bonds are of different activity. Compared with most vinyl monomers, the typical allyl monomers are low activite in the radical polymerization due to the degradational chain transfer to monomer. In the course of polymerization the labile H atom in the α-position to the double bond is eliminated and a stable allyl radical is formed. As a consequence, the kinetic chain is terminated and the process stops [9]. On the other hand, fullerene is highly active toward the allyl radicals: the rate of reaction of C_{60} with low active allyl radicals is higher than with methacrylate ones [10, 11]. As a result, the number of fullerene included in the polymer chain of allyl methacrylate is by an order of magnitude higher than in the case of poly(methyl methacrylate) [10].

Fullerene exhibits both stabilizing and accelerating effect with respect to the thermal decomposition of the polymer. Thus, the thermal stability of polystyrene grafted to the C_{60} is significantly reduced [12]. The formation of a covalent bond between C_{60} and the polymer chains leads to a reduction of its heat resistance by more than 100°C. The process is initiated by thermal cleavage of the weak bond in the β-position to the C_{60}. However, the thermal stability of poly (methyl methacrylate), which was synthesized by radical polymerization in a mixture with fullerene, on the contrary, increases. Fullerene suppresses the low-temperature stage of decomposition of the polymer, increasing thereby its thermal stability.

The purpose of this work is to examine patterns of the (co)polymerization reactions that underlie the preparation of a branched poly(methyl methacrylates) containing covalently bound fullerene and to investigate the influence of fullerene on the structure and properties of the resulting copolymers. In this connection we compared the kinetics of the (co) polymerization of the monomer **I** with multifunctional comonomers **II** and **III** in the absence and the presence of fullerene, as well as physicochemical characteristics and thermal stability of the obtained copolymers.

Radical copolymerization of methyl methacrylate and multifunctional monomers and analysis of the copolymerization products. Figure 1 shows the kinetic curves of (co)polymerization of monomer **I** in toluene. Homopolymerization of monomer **I** proceeds without the gel effect, the reaction rate decreases with consumption of the initiator and monomer in the reaction mixture (Fig. 1a, curve *1*). At the copolymerization of monomers **I** and **II** there is a weak gel effect, but it is completely absent at the copolymerization of monomers **I** and **III** (Fig. 1b). The disappearance of the gel effect at the three-dimensional radical polymerization of multifunctional monomers is usually due to the suppression of cross-linking reactions [2].

The difference in the rates of copolymerization (Fig. 1b, curves *1* and *2*) is due to the chain transfer to monomer **III**. The IR spectroscopic analysis of the structure of the polymer obtained by polymerization of monomer **III** in toluene confirms this conclusion. The attention is drawn to the absence in its IR spectrum of the absorption bands associated with the bending vibrations of H atoms in the $H_2C=C(CH_3)$ and $H_2C=CHCH_2$ groups of the monomer. However, the absorption bands are observed that correspond to the bending vibrations of the H atom in the =CH group. This indicates the reaction of chain transfer to the allyl group of the monomer. As a consequence, a part of the double bonds of the allyl groups is not involved in polymerization, as evidenced by the presence of absorption band at ~1646 cm^{-1}. The homopolymer is insoluble and has a network structure, which is due to the involvement of both $H_2C=C(CH_3)$ and $H_2C=CHCH_2$ groups in the three-dimensional radical homopolymerization.

The copolymerization of monomers **I** and **III** in the presence of 1-decanethiol is accompanied by chain transfer reaction, which leads to a slight decrease in the reaction rate. A comparison of curves *2* and *3* in Fig. 1b shows that the efficiency of chain transfer to monomer **III** is higher than to the thiol. The growth of polymer chains involves mainly more active methacrylate groups of monomer **III**. Conversion of double bonds in the copolymers obtained by copolymerization of the monomers **I** and **III** in the absence and presence of the thiol is close to 100%, according to the intensity of the absorption bands of stretching vibrations of C=C bond at ~1646 cm^{-1} in the IR spectrum.

The changes in the kinetics of three-dimensional radical (co)polymerization are reflected in the structure of the resulting copolymers. For example, the copolymer prepared from the monomers **I** and **II**, had a network structure and is insoluble. The copolymers prepared from monomers **I** and **III** in the absence and presence of thiol, are soluble. The reason of it is an intensive chain transfer to monomer **III**, leading to limited growth of polymer chains, reducing their length and suppressing the cross-linking reactions [9].

At the copolymerization of the monomers **I** and **II** having almost the same reactivity of the methacrylate groups ($r_1 = r_2 = 1$) [13], the copolymer is formed with the composition corresponding to that of the initial reaction mixture. Microstructure of copolymers containing the units **III**, judging by the copolymerization constants that are equal to $r_{\text{monomer I}} = 1.01\pm0.46$ and $r_{\text{monomer III}} = 0.79\pm0.35$ [11], differs from that of the copolymers containing the units **II**. The participation of the pendant C=C bonds in the side chains of bifunctional comonomers in radical copolymerization leads to the formation of macromolecules having a branched structure.

Based on this pattern of the radical (co) polymerization of monomer **I**, we performed a targeted synthesis of the copolymers with different contents of units **II** and **III**. When the molar ratios methyl methacrylate : dimethacrylate : decanethiol was equal to 100:5:5 or 100:21:21 the topological structure of copolymers was significantly different. This is seen from the values of the primary polymer chain length, calculated using the equation $L \approx k_p([M_1] + [M_2])/(k_t [R])$, where k_p and k_t are the rate constant of the chain propagation and transfer, respectively; $[M_1]$ and $[M_2]$ are the concentration of the monomers **I** and **II**; [R] is the concentration of the transfer agent [13]. In calculating the L values k_p k_t values at 60°C were taken equal to 834 and 300 l mol^{-1} s^{-1}, respectively [13, 16]. In the case of copolymers with a low concentration of monomer **II** the longest primary chains polymer chains (L ~ 58) were produced. In the copolymer with high content of **II** the value of L is reduced to 16 monomer units, of which ~3 units belong to the branching agent. The copolymer obtained at a high concentration of monomer **II** is characterized by short primary and chains between branching points and a large number of terminal chains. At the fractionation using different precipitants several fractions were isolated from it significantly differing in the degree of branching, molecular weight, intrinsic viscosity, and glass transition temperature [17]. Thus, the copolymers are the products of non-uniform structure.

Table 1 lists the yields of the copolymers. The attention is drawn to a significant increase in the proportion of fraction 2 in the copolymer obtained at a high content of monomer **III** in the reaction mixture. Thus, a 4-fold increase in the concentration of the latter in the reaction system leads to a 2.5-fold increase in the content of this fraction. As a consequence, the main reaction product is a low molecular weight copolymer.

The IR spectra of both fractions of copolymers containing monomer units **III** contain similar absorption bands associated with vibrations of various groups. However, there are some differences. Thus, in

Table 1. Yield of copolymers based on monomer **I**

Copolymer	Co-monomer	Molar ratio of **I/II**, **III**/transfer agent	Yield, %	
			fraction 1	fraction 2
Usual With fullerene	**I**	100:5:5	76.0 65.2	–[a] –[a]
Usual With fullerene	**II**	100:21:21	66.2 65.7	–[a] –[a]
Usual With fullerene	**III**	100:5:5	63.4 66.0	9.2 8.5
Usual With fullerene	**III**	100:21:21	25.1 19.4	42.8 62.7

[a] Yields of low molecular weight fractions was not measured.

the region of 700–800 cm^{-1} the spectrum of the fraction 2 of copolymer with a small number of monomer units **III** contains along with the band at 752 cm^{-1} related to the pendulum vibrations of CH_2 groups of the main chain, the absorption band of low intensity at 724 cm^{-1}. In the IR spectrum of the fraction 1 it is present as a shoulder. In addition, in the IR spectrum of fraction 2 the intensities of absorption bands belonging to stretching vibrations of H atoms in the region of 2800–3000 cm^{-1} are redistributed, in particular, the intensity of the absorption bands of methylene groups at $\nu = 2926$ cm^{-1} increases compared with the fraction 1. A 4-fold increase in the content of the monomer units **III** and thiol residues in the copolymer leads to the increase in the intensity of the absorption bands of methylene groups in these areas in the IR spectra of both fractions. These changes in the IR spectra can be associated with the inclusion of the residues of the chain transfer agent, the groups $C_{10}H_{21}S$, in the polymer chains due to the chain transfer.

According to IR spectroscopy, the obtained copolymers contain unreacted double bonds. In copolymers containing monomer units **II** they correspond to the pendant C=C bonds of the methacrylate groups: their stretching vibrations appear at $\nu = 1638$ cm^{-1}, and the bending vibrations of H atoms in the $(CH_3)C=CH_2$ group, at $\nu = 812$ cm^{-1}. The IR spectra of both fractions of the copolymer with high content of monomer units **III** have absorption bands corresponding to stretching vibrations of the double bond in the allyl group at ~1646 cm^{-1} and bending vibrations of the H atom in the group $CH=CH_2$. Their content was estimated to be higher in the copolymer fraction 2.

The features of the structure of the copolymers obtained were evaluated by analyzing the physicochemical characteristics sensitive to the architecture, like molecular weight, polydispersity, viscosity parameters, the content of pendant C=C bonds, and the glass transition temperature.

Figure 2 shows the curves of the molecular weight distribution of linear poly(methyl methacrylate) and copolymers, constructed according to the data of a refractometry detector. It is seen that in contrast to the linear polymer, the curve of a copolymer containing units of the monomer **II** is polymodal (Fig. 2a, curve *2*). After the copolymerization of the monomers **I** and **III** we succeeded to isolate from the reaction mixture a narrow fraction of the copolymer (Fig. 2b, curve *1*). Table 2 shows the absolute and relative values of the weight average molecular weight (M_w) and polydispersity ratios (M_w/M_n) of copolymers. As seen, the absolute values of M_w of copolymers with a small number of monomer units **II** is ~1.6 times lower, and the polydispersity ratio is higher than those for the linear polymer where $M_w = 17.4\times10^3$, and $M_w/M_n = 1.9$. However, with increasing content of monomer units **II** in the copolymer the value of M_w increases and becomes comparable with the M_w of the linear polymer, and M_w/M_n increases more than twice. The molecular weight of the fraction 1 of the copolymer containing the units of the monomer **III**, as expected, is lower than that of the copolymer with the units of the monomer **II**: it decreases with increasing content of the co-monomer and the transfer agent units.

The copolymer structure, the degree of branching and molecular weight affect the behavior of macromolecules in solution. The peculiarity of branched polymers is a compact conformation of the macromolecules and, consequently, low values of intrinsic viscosity [18]. The viscosity parameters of the

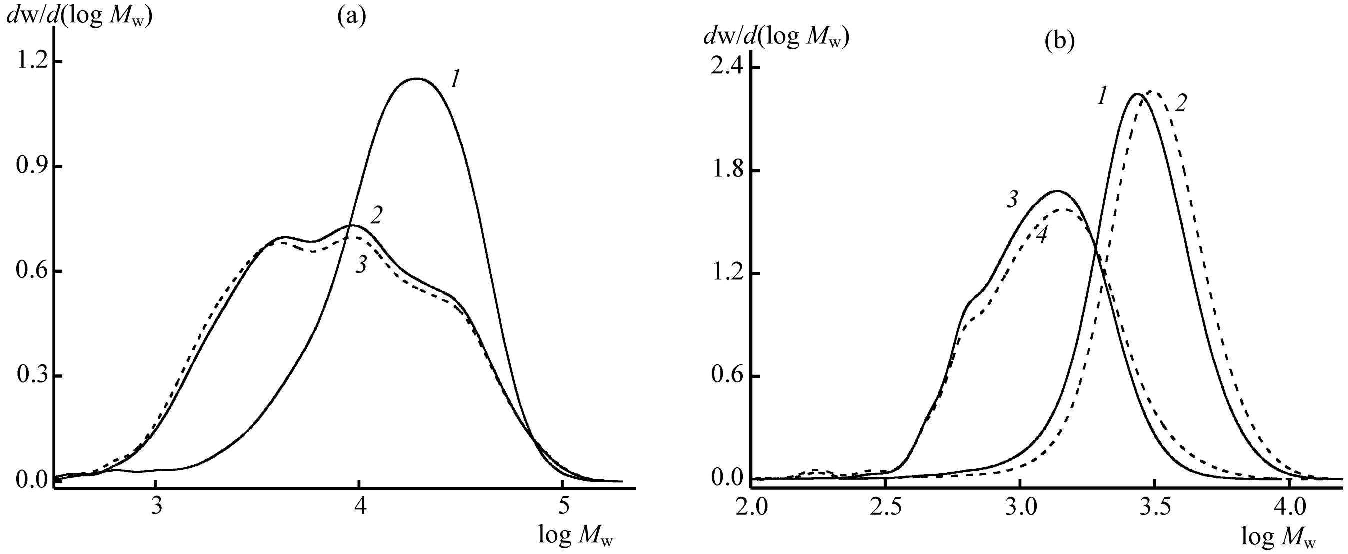

Fig. 2. The curves of the molecular weight distribution: (a) of linear poly(methyl methacrylate) (*1*), usual (*2*) and fullerene-containing (*3*) of copolymers with high content of monomer **II** units; (b) fraction 1 (*1, 3*) and fraction 2 (*2, 4*) of usual and fullerene-containing copolymers, respectively, with a high content of monomer **III** units.

obtained copolymers are shown in Table 2. Intrinsic viscosity of the copolymers with the monomer **III** units is lower compared with the copolymers containing the monomer **II** units. Increasing the number of monomer **II** units in the copolymers does not affect the [η] and *k*' values. The constancy of [η] with increasing molecular weight of the copolymer should obviously be seen as a result of lowering the Mark–Kuhn–Houwink parameter associated with the conformation of macromolecules. Thus, a copolymer with a high content of monomer **II** units is more branched than the copolymer with low content of dimethacrylate.

Table 2. Physicochemical characteristics of the copolymer based on monomer **I**

Copolymer	Co-monomer	Molar ratio of **I**/**II**, **III**/ transfer agent	$M_w \times 10^{-3}$ [a]	M_w/M_n	Viscosity parameters		[C=C], mol kg^{-1}	T_g, °C
					[η], dl g^{-1}	*k*'		
Usual	**II**	100:5:5	10.6/10.4	2.6/2.2	0.055	1.4	0.3	73.8
With fullerene			13.5/10.1	1.7/2.2	0.05	1.9	0.36	67.4
Usual	**II**	100:21:21	17.2/14.2	4.3/3.2	0.053	1.4	0.86	34.3
With fullerene			19.2/13.9	3.2/3.4	0.057	0.9	0.83	34.2
Usual	**III**	100:5:5						
Fraction 1			4.6/5.3	1.5/1.4	0.042	1.9	0.83	61.8
Fraction 2			1.1/1.4	1.3/1.3	–	–	1.76	–25.2
With fullerene	**III**							
Fraction 1			8.8/5.3	1.4/1.5	0.045	1.3	0.95	68.0
Fraction 2			2.5/1.3	3/1.3	–	–	1.78	–25.2
Usual	**III**	100:21:21						
Fraction 1			2.5/3.1	1.3/1.3	0.04	0.9	2.33	30.4
Fraction 2			1.0/1.4	1.3/1.3	0.026	0.9	3.27	–51.7
With fullerene								
Fraction 1			5.7/3.5	5.4/1.4	0.038	1.0	2.3	29.4
Fraction 2			3.2/1.5	1.6/1.2	0.029	0.8	3.15	–52.2

[a] The numerator is the molecular weight and polydispersity, according to the GPC coupled with light scattering, the denominator is GPC data (detector refractometer).

The growth of the content of the monomer **III** units in the copolymer is accompanied by a noticeable decrease in the *k*' values. The polymer coils of this copolymer are well swelling in toluene like those of the linear polymer, for which the value of *k*' = 0.8. The constancy of the [η] values in view of lowering the molecular weight of the copolymer appears to be associated with an increase in the value of the Mark–Kuhn–Houwink parameter. The copolymer with a high content of monomer **III** units probably is characterized by a lower degree of branching than the copolymer with a low content of **III** units, and its behavior in solution is close to a linear polymer. The reason for reducing the degree of branching of the polymer, apparently, is a significant increase in the contribution of chain transfer to monomer.

An increase in the monomer **II** or **III** content in the initial mixture leads to an increase in unsaturation of the resulting copolymers (Table 2). This is due to an increase in the concentration of the chain transfer agent in the reaction mixture, which limits the growth of polymer chains. The copolymers with the monomer **III** units contain more C=C bonds. Their concentration in the fraction of the copolymer with a low number of monomer **III** units is ~3 times higher than in the copolymer comprising the monomer **II** units. This seems to be caused by a significant contribution of chain transfer to the monomer. Moreover, the content of the C=C bonds in the fraction 2 of the copolymer is almost 2 times higher than in fraction 1.

It follows from the data on T_g (Table 2) that in the copolymer with low content of monomer **II** units at 73.8°C the segmental mobility of polymer chains defrosts, and the α-transition occurs. The decrease in T_g is apparently due to an increase in the polydispersity of the macromolecules and the number of terminal chains in them. The 4-fold increase in the monomer **II** units reduces the value of T_g of the copolymer to 40°C due to further growth of the number of terminal chains in it.

The copolymer with a small number of monomer **III** units has a T_g by 10°C lower than the copolymer with the same number of monomer **II** units, apparently as a result of reducing its molecular weight. The attention is drawn to a significant difference between the values of T_g of the fractions of this copolymer due to the difference in their molecular weights and physical states. Fraction 2 of the copolymer prepared from monomers **I** and **III** is a highly viscous liquid, its T_g value falls to the region of subzero temperatures. Further increase in the content of units **III** in the copolymers, as well as in the case of the copolymers of **I** with **II** of the same composition is accompanied by a decrease in the value of T_g by ~30°C and increase in segmental molecular mobility of poly-mer chains, probably as a result of lower molecular weight of the polymer.

Radical copolymerization of methyl methacrylate and multifunctional monomers in the presence of fullerene and analysis of the fullerene-containing products. In the radical (co)polymerization of vinyl(idene) monomers fullerene exhibits inhibitory properties [5, 19], which depend on the nature of monomers, or, more specifically, on the reactivity of the corresponding radicals. Fullerene reacts both with the initiator radicals formed at its thermal decomposition, and with the radicals of the chain growth. The reaction of fullerene with the radical of the initiator azobisisobutyronitrile in toluene proceeds with a high rate at a molar ratio of [C_{60}]:[initiator] equal to 1:20. The degree of conversion of free C_{60} in 100 min at 60°C is ~50% [20]. At adding 1-decanethiol to the initiator–C_{60} fullerene mixture the degree of conversion decreases due to the competitive reaction between the radical initiator and transfer agent, and the amount of radical initiator involved in the reaction with C_{60} reduces. Adding (di)vinyl monomers in the system of C_{60}–initiator or C_{60}–initiator-transfer agent leads to an increase in the degree of the fullerene conversion [20].

Figure 1a, curves *2* and *3*, shows the kinetic curves of polymerization of monomer **I** in toluene in the whole range of conversions in the presence of fullerene and of its adduct obtained by the addition of the radicals formed at the thermal decomposition of azobisisobutyronitrile to the C_{60} double bonds [21]. In the presence of fullerene the curves $C = f(t)$ become *S*-shaped and the polymerization rate decreases (Fig. 1a, curve *2*). This indicates that fullerene inhibits polymerization of monomer **I** reacting with the growing methacrylate radicals. Thus, fullerene behaves as an inhibitor of polymerization of monomer **I** in toluene. According to [22], the rate constant k_x of inhibition by fullerene of monomer **I** polymerization is almost higher than the growth rate constant k_p by an order of magnitude.

However, the fullerene adduct with the ~14 added cyanoisopropyl radicals has no effect on the kinetics of polymerization, and the curves *1* and *3* (Fig. 1a) almost completely coincide. The fullerene adduct obtained at a molar ratio of [C_{60}]:[initiator] = 1:13 [21] is inert in the radical polymerization of the monomer **I**. The reason for this is obviously a lack of available active centers on fullerene. However, it can be assumed that the adducts with a smaller number of connected radicals formed *in situ* in the radical process, as well as the free fullerene, slow down the monomer **I** polymerization.

Kinetic curves of copolymerization of monomer **I** with bifunctional monomers in the presence of fullerene changed significantly and become of *S*-shaped nature due to the inhibition of polymerization by fullerene and its products (Fig. 1b, curves *4*, *5*). Effectiveness of fullerene as the inhibitor of copolymerization of the monomers **I** and **II** is lower compared with the copolymerization of the monomers **I** and **III**. In favor of this statement points a somewhat higher rate of copolymerization of the monomers **I** and **II**. These data are consistent with the results of [10] where the slowing of copolymerization of the monomers **I** and **III** initiated by benzoyl peroxide in the presence of fullerene has been discovered. In the absence of fullerene with 10 mol % of the monomer **III** in the reaction mixture insoluble cross-linked products were obtained at the 9% conversion, while in the presence of fullerene the gel point shifted to higher conversions. Due to the high activity of the fullerene toward the allyl radical a transition from the degradation (in the absence of C_{60}) to the effective chain transfer on the monomer occurs. As a result of interaction of allyl radicals with C_{60} a product with the lack of conjugation formed. It behaves as a co-monomer and participates in the formation of the chain at the early stages of the conversion, therefore the proportion of allyl addition increases [11]. However, in the copolymerization of monomers **I** and **III** a substantial increase in the proportion of effective chain transfer can hardly be expected, as the reaction mixture contains a large excess of 1-decanethiol, which competes with the fullerene for radicals.

At the (co)polymerization of monomer **I** in the presence of fullerene a singlet signal was observed in the ESR spectrum (Fig. 3a). This spectrum is due to the fullerene radical formed by the interaction of polymer radicals with fullerene. At the polymerization of all three reaction mixtures the curves of accumulation of radicals include an induction period. Probably the fullerene radicals are rapidly consumed not reaching the steady-state concentration. This effect is more pronounced in the polymerization of monomers **I** and **III**, probably due to increased activity of the fullerene with respect to the allyl radicals. At the (co)polymerization of monomer **I** the concentration of fullerene radical increases rapidly and reaches saturation (Fig. 3b). The limiting concentration of the fullerene radicals is higher at the copolymerization of monomer **I** with **II** or **III**, than at its homopolymerization. After the completion of (co)polymerization stable radicals are recorded.

The state of the fullerene in the homopolymerization of monomer **I** in toluene was monitored by means of UV spectroscopy. The optical density of the absorption band of fullerene at λ_{max} ~ 330 nm decreased with time. In the reaction mixture after ~5 h free fullerene was still present and an absorption appeared in the region of 450 nm characteristic of covalently bound fullerene. Fullerene remained in free form even after ~8 h of the reaction. Only to the end of polymerization fullerene was bound to the polymer chains almost completely.

For analytical purposes we synthesized specially the fullerene-containing copolymers of different composition. The data in Table 1 show that in the copolymerization of monomers **I** and **III** in a molar ratio of the reagents 100:5:5 fullerene has virtually no effect on the yield of final products. However, at the molar ratio of reactants 100:21:21 the proportion of fraction 2 in the polymer product increases.

The IR spectra of fullerene-containing copolymers do not contain the characteristic absorption bands of free fullerene at ν 525 and 575 cm^{-1} [23]. A comparison of the IR spectra of normal and fullerene containing copolymers obtained at a deep conversion shows that fullerene has no significant effect on their molecular structure, and characteristics of the latter are by a set of reactions, including the growth, termination, and chain transfer to 1-decanethiol and monomer **III**.

Addition of fullerene to the polymer chains is seen also from the data of UV spectroscopy. At the interaction of fullerenes with radicals of various types the double bond in the fullerene core is broken and its electronic state is changed. As a consequence, the spectrum of the free fullerene (Fig. 4) is transformed. In the UV spectra of the fullerene copolymer the absorption band of the fullerene at 330 nm disappears. In addition, in the UV spectrum of the copolymer with a high content of monomer units **III** (Fig. 4b) a strong

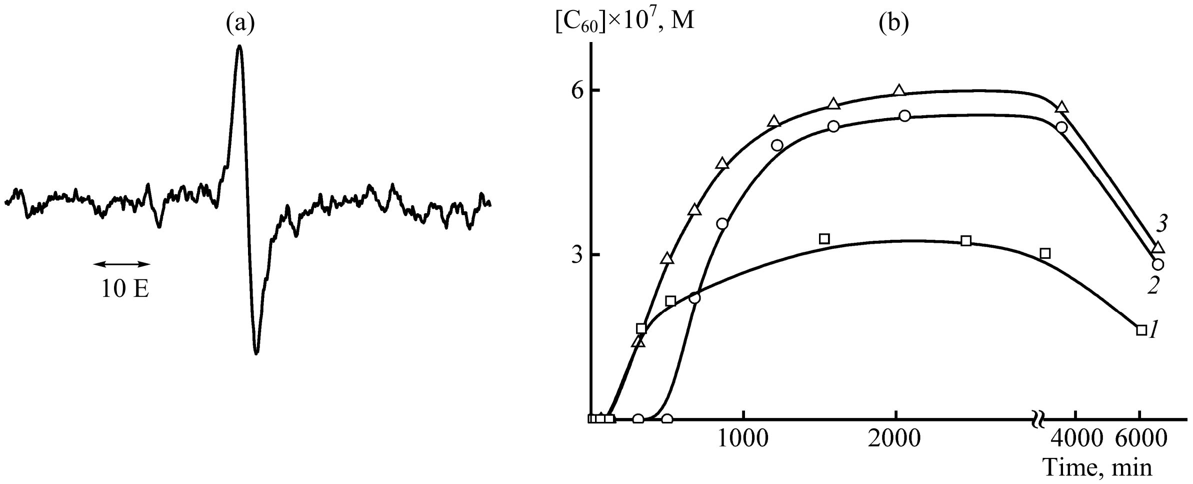

Fig. 3. (a) ESR spectrum observed at the copolymerization of the monomers **I** and **III** in the presence of 1-decanethiol, $T = 20°C$. (b) The kinetics of accumulation of fullerene radicals at the homopolymerization of monomer **I** (*1*) and at its copolymerization with **III** (*2*) and **II** (*3*) in the absence (*1*) and in the presence of 1-decanethiol (*2, 3*). The molar ratio of [monomer **I**]:[monomer **II**, **III**]:[1-decanethiol] = 100:5:5, [Initiator] = 2×10^{-2} M, $[C_{60}] = 0.78\times10^{-3}$ M, [Toluene] = 80 wt %, $T = 60°C$.

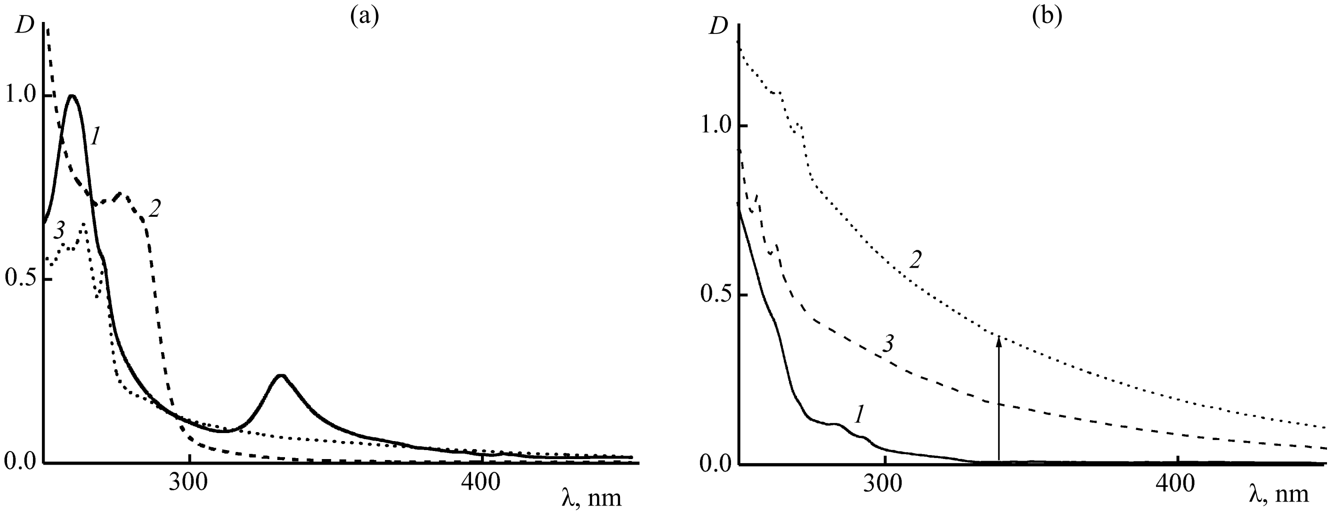

Fig. 4. (a) UV spectra of fullerene (*1*), usual (*2*) and fullerene-containing (*3*) copolymers with high content of the monomer **II**; concentration of copolymers in chloroform: 1.7 g l^{-1} and 0.84 g l^{-1}, respectively. (b) UV spectra of fraction 1 (*1*) of usual copolymers and fractions 1 (*2*) and 2 (*3*) of the fullerene-containing copolymers with high content of monomer **III** units. Concentration of copolymers in chloroform: 3.5, 1.7, and 3.5 g l^{-1}, respectively. The thickness of the cell 1 cm.

absorption appears in the long wavelength region, indicating the increase in the number of radicals added to fullerene as compared with the copolymers with monomer **II**. However, in both cases the macromolecule appears to be nonuniform with respect to the fullerene content.

At the copolymerization of monomer **I** in the presence of fullerene the topological structure of copolymers formed is changed: the length of primary polymer chains shortens, and due to the termination of polymer radicals on the fullerene multiple active sites (double bonds) the macromolecules appear containing the fragments of branched and star-shaped structures with the fullerene itself is located in the sites of the branching. The fullerene copolymers composition and structure are probably even more complex compared with the conventional copolymers. As a consequence, we can expect a change in their physicochemical parameters.

Figure 2a, curves *2* and *3* shows that the low molecular weight component of the molecular weight distribution (MWD) curve of the fullerene-containing copolymer with the monomer **II** units is slightly shifted toward lower molecular weights compared to the MWD curve of conventional polymer of the same composition. In general, the shapes of the MWD curves of the copolymers are almost identical. The MWD curves of the two fractions of fullerene-containing copolymer with the monomer **III** units are slightly shifted toward higher molecular weights (Fig. 2b, curves *3* and *4*) compared with the MWD curve of the conventional copolymer. Fractionation of fullerene-containing copolymer with monomer **III** units also gives a narrow fraction (Fig. 2b, curve *2*). The data in Table 2 show that the molecular weight of conventional and fullerene copolymer determined by gel permeation chromatography (GPC) are practically identical. The molecular weight of the fullerene-containing copolymer obtained from GPC data in combination with light scattering should be regarded as estimates. Aggregation of the fullerene-containing macromolecules in a polar eluent [24], as well as the absorption of a part of incident light by the fullerene molecule, apparently, leads to a distortion of the results of molecular weight determination.

In fullerene copolymer with monomer **II** units the value of the intrinsic viscosity varies slightly, in contrast to the Huggins constant (Table 2). Compared to conventional copolymer it grows in the fullerene-containing copolymer with a low concentration of monomer **II** and then decreases to a value close to that in the linear polymer when the copolymer contains much dimethacrylate. The diminishing of the k' value evidences better thermodynamic affinity of the fullerene-containing copolymer of this composition to toluene, and a higher degree of swelling of its macromolecules, probably not only due to the increase in their hydrophobicity, but also thanks to reduced degree of branching.

Adding the C_{60} molecules to polymer chains of the copolymer with a small number of monomer **III** units also has little effect on the value of intrinsic viscosity. Compared to conventional copolymer of same composition, its k' value is reduced ~1.5-fold. Meanwhile, the viscosity parameters of fullerene-containing copolymer with a high content of monomer **III** units remain virtually unchanged. In the first case the polymer coils strongly swell in toluene, probably due to their lower molecular packing density and greater hydrophobicity. The swelling of polymer coils of the fullerene-containing copolymer with a high content of monomer **III** units is practically unchanged compared to the conventional copolymer of the same composition.

The data in Table 2 show that fullerene almost does not affect the unsaturation of the investigated copolymers. As in the case of conventional copolymers, the content of C=C bonds in the fullerene-containing copolymers is determined by the content and structure of the multifunctional comonomers. The macromolecules of the fractions 2 in the fullerene copolymers with monomer **III** units are characterized by a higher content of “pendant” C=C bonds than those of the fractions 1 of the copolymer regardless of composition.

Fullerene differently affects the T_g of obtained copolymers. The T_g of fullerene-containing copolymer with a low concentration of monomer **II** is reduced by ~7°C as compared to conventional copolymer of the same composition. Decrease in T_g may be due to an increase in the number of their free-end chains, for example, due to the increasing proportion of the star-shaped macromolecules. Meanwhile, the segmental molecular mobility of the chains of usual and fullerene-containing copolymer with high content of monomer **II** units is the same, as evidenced by their T_g values.

Adding fullerene does not affect the T_g value of the fraction 2 of the copolymer with low content of units of monomer **III**. However, it increases slightly in the fraction 1 of copolymer. The T_g values of both fractions of the fullerene-containing copolymer with a high content of **III** units are almost the same as in the case of an ordinary copolymer of the same composition. Thus, the segmental molecular mobility of polymer chains of the investigated copolymers depends on the content of the branching agent and its chemical structure. In copolymers with low content of bifunctional monomer the fullerene embedded in the polymer chain serves as an additional factor affecting the rigidity of the polymer chains.

Thermal stability of copolymers and their fullerene analogs. Effect of 1-decanethiol and structure of macromolecules on the thermal stability of the investigated copolymers was evaluated by comparing the mass loss curves of linear polymers and copolymers. Then the mass loss curves of copolymers and their fullerene analogs were compared.

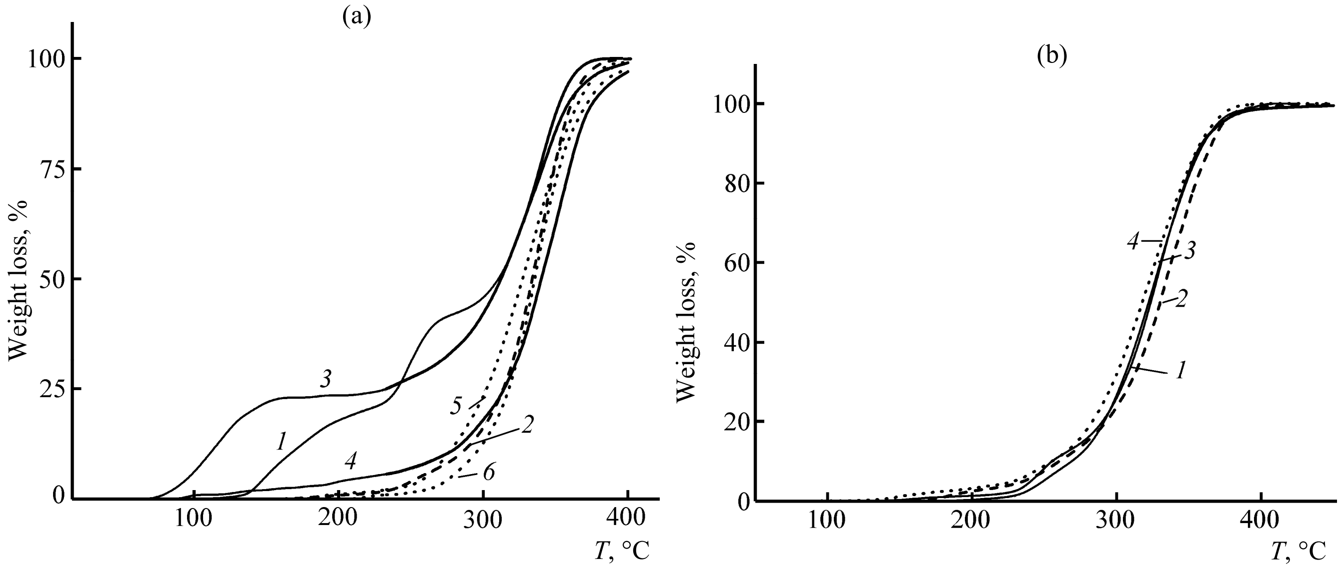

Fig. 5. (a) Kinetics of the non-isothermal decomposition of the linear poly(methyl methacrylate) obtained in the absence (*1*) and in the presence of 1-decanethiol (*2*), and usual and fullerene-containing copolymers with a low (*3, 4*) and high (*5, 6*) content of the monomer **II** units (weighed samples 8–10 mg). (b) Kinetics of the non-isothermal decomposition of usual and fullerene-containing copolymers with a low (*1, 2*) and high (*3, 4*) content of the monomer **III** units (weighed samples 9–10 mg). Heating rate 4 deg min^{-1}.

Figure 5a shows the curves of mass loss of linear poly(methyl methacrylate) obtained in the absence and in the presence of 1-decanethiol, as well as fractions 1 of usual and fullerene-containing copolymer with monomer **II** units. The linear polymers differ by molecular weight. The polymer obtained in the absence of 1-decanethiol had $M_n = 11.8\times10^3$ and $M_w = 22.0\times10^3$, and the polymer synthesized in the presence of 5 mol % of 1-decanethiol had $M_n = 3.4\times10^3$ and $M_w = 4.6\times10^3$. The decomposition of the linear poly (methyl methacrylate) (curve *1*) proceeds in three stages. In the first low-temperature stage (120–230°C) the weight loss was ~21%. It seems to be associated with the rupture of defective bonds in the main chain, resulting from addition of monomer units of *head to head* type, and with the depolymerization of the formed radicals [25, 26] with the release of methyl methacrylate. The weight loss by the linear polymer in the second stage of thermolysis (230–275°C) is comparable to that of the first stage (~21%) and is due to the rupture of β-bonds in the terminal units containing C=C bond formed by the termination of polymer chains through disproportionation. At the polymerization of monomer **I** in solution this mechanism is responsible for the termination of up to 80% of the radicals [27]. The third, a high-temperature stage of the thermal degradation of linear polymer, is realized in the temperature range 290–360°C and is caused by rupture of C–C bonds in the main chain. At this stage the weight loss is 58.6%. It should be noted that the syndiotactic and isotactic polymethyl methacrylate obtained by anionic polymerization have no defects in the chain and give the unimodal peaks at the thermal degradation [28].

As a result of chain transfer, the linear polymer is formed with shorter chains, some of which include at the end the $SC_{10}H_{21}$ residues of 1-decanethiol. This leads to a change in the mechanism of its thermal degradation (Fig. 5a, curve *2*). The low-temperature phase is suppressed: the first low-temperature stage (175–240°C) is practically absent, probably due to the decrease in the number of *head to head* units in the shorter macromolecule. The polymer loses only 1.4% of its weight. The suppression of the second low-temperature stage (240–280°C) is apparently due to a decrease in the concentration of the terminal C=C bonds by reducing the contribution of the disproportionation reaction in the termination of polymer chains. The weight loss by polymer is 7%. The main mass loss, 91.6%, falls on the third stage (280–430°C). And the second and third stages are poorly resolved. Thus, a linear polymer with lower molecular weight is thermally more stable than the polymer obtained in the absence of the chain transfer agent.

Analysis of the curve *3* in Fig. 5a*,* shows that the introduction of a small number of monomer **I** units and 1-decanethiol residues into the copolymer composition leads to acceleration of the decomposition process. The process proceeds in two stages. In comparison with the linear polymer, the first stage occurs in a lower temperature range (70–160°C). In this case there is no second stage which typically occurred in the case of the linear polymer. Its absence is probably due to the change in the mechanism of termination of the polymer chains. Thus, the branching accelerates the thermal decomposition of the copolymer of this composition.

The increase in the comonomer of units **II** and residues of 1-decanethiol results in 4-fold suppression of the low-temperature phases, characteristic of the thermolysis of the copolymer with low content of the branching agent, pointing to its higher thermal stability (Fig. 5a, curve *5*). This is probably due to the change in the topological structure of the copolymer, namely, to a decrease in the length of the internodal and terminal chains, as well as changes in the mechanism of termination of the polymer chains.

Figure 5b shows the curves of the weight loss by the copolymers with monomer **III** units. In the copolymer with low content of these units there are three stages of thermal decomposition: in the initial stage at 140–220°C the copolymer loses only 1.8% of its weight, in the second stage, in the range 220–260°C, the amount of volatile products increases and the weight loss is 11.9%. The main weight loss of 86.3% occurs in the high-temperature stage (260–450°C). Thus, the nature of the co-monomer affects significantly the thermal properties of the resulting products. The copolymer with low content of monomer **III** units is thermally more stable than the copolymer with the same number of units of the monomer **II**. With increasing content of co-monomer units and 1-decanethiol residues in the copolymer the two-stage degradation process is maintained. The poorly resolved stages correspond to the temperature ranges 190–260°C and 260–415°C.

The process of decomposition of the linear poly (methyl methacrylate) is suppressed by many polycyclic structures, including the grafted anthracene (880 units of the monomer **I** per one anthracene unit). Fullerene covalently bonded to polymethacrylate chains also exhibits a stabilizing effect [28]. Curve *4* in Fig. 5a shows that the inclusion of fullerene in the polymer chains of the copolymer with low content of comonomer **II** units shows the same effect on the thermal decomposition of the linear polymer as 1-decanethiol: it suppresses the low-temperature phase, while shifts the high-temperature phase to higher temperatures. The thermolysis of fullerene-containing copolymer, in contrast to conventional one, includes a poorly expressed low-temperature stage of the release of volatile products. The weight loss in the range 100–180°C does not exceed 2.5%. A noticeable rate of degradation corresponds to the temperatures above 210°C. The process ends at T = 400°C by almost complete weight loss. Comparison of the kinetic curves *3* and *4* in Fig. 5a*,* suggests a higher thermal stability of fullerene-containing copolymer as compared to a nonfunctionalized one. The macro radicals formed in the initial stages interact rapidly with the double bonds of the covalently bound fullerene and therefore have no time to depolymerize. The energy of the newly formed bond appears to be no lower than the energy of C–C bond of the main chain. In the copolymer of this composition a high enough number of active sites seems to occur in the grafted fullerene to manifest its inhibitory effect.

The curve of mass loss at the thermolysis of fullerene-containing copolymer with a high content of monomer **II** units (Fig. 5a, curve *6*) has no low-temperature stage of formation of volatile products. In the case of copolymers of this composition somewhat higher thermal stability is also seen in the fullerene-containing copolymer. A noticeably high degradation rate is observed at T above 190 and 210°C. The number of active reaction sites in fullerene and their availability for interaction with macroradicals in this copolymer probably decrease. As a consequence, the inhibitory effect of fullerene is much less expressed than in the decomposition of the fullerene-containing copolymer with low content of monomer units **II**.

Figure 5b shows that the incorporation of fullerene into the polymer chain of the copolymer with a low content of the monomer **III** leads to a two-stage process, the curves reflect two poorly resolved stages in the usual temperature ranges 170–230°C and 230–390°C, corresponding to 4.5 and 95.5% weight loss, respectively. The main stage is somewhat shifted to higher temperatures. Thus, the fullerene-containing copolymer in the low temperature region loses more weight than usual copolymer, in the high-temperature occurs inverse picture, probably as a result of termination of macroradicals in the active sites of the grafted fullerene, whose number is significantly lower than in the fullerene-containing copolymer of the same composition with the monomer **II** units.

The decomposition of the fullerene-containing copolymer with a high content of the monomer **III** units occurs in a single stage, but it begins at *T* above 140°C. This means that the copolymer is thermally less stable than the usual copolymer. Probably, in the copolymer with high content of monomer **III** units a high proportion of allyl type connections to fullerene is present, which leads to a decrease in the number of free active sites capable of stabilizing the process of destruction. Thus, in going from linear to branched macromolecules the nature of thermal degradation is changed and low-temperature phase is suppressed. Branched macromolecules containing covalently bound fullerene in most cases are thermally more stable than the nonfunctionalized counterparts.

The results of these studies show that by the three-dimensional radical copolymerization of methyl methacrylate and multifunctional monomers in the presence of 1-decanethiol and fullerene dissolved in toluene copolymers can be obtained containing covalently bound fullerene. Their topological structure and physicochemical characteristics are determined by the monomer : multifunctional co-monomer : chain transfer agent ratio, as well as by the rate constants of growth, termination, and chain transfer and the structure of the multifunctional co-monomer. The copolymers with high content of monomer **III** units can be obtained, apparently, also at a lower concentration of transfer agent in the reaction mixture, as a result of an additional reaction, which limits the growth of polymer chains, namely, the chain transfer to monomer. Fullerene copolymers are of interest as new hybrid materials that combine the unique properties of the polymer component of the branched structure and valuable physical and chemical properties of fullerene.

EXPERIMENTAL

Monomer **I** (Aldrich) was purified by distillation in a vacuum. Other reagents: monomer **II,** the triethylene glycol dimethacrylate (Aldrich, 95%), monomer **III,** the allyl methacrylate (Aldrich), and 1-decanethiol (Alfa Aesar, 96%) were used without pretreatment. Initiator azobisisobutyronitrile was purified by recrystallization from ethanol. Toluene was distilled before use. In this paper we used the C_{60} fullerene with the content of the basic substance ~ 99.95% from Fullerene-Center, Nizhnii Novgorod.

Branched poly(methyl methacrylate) was prepared using three-dimensional radical copolymerization of the monomer **I** with the monomers **II** or **III** in toluene in the presence of 1-decanethiol by the method of [2]. Synthesis conditions: the molar ratio [monomer **I**]:[monomer **II**, **III**]:[1-decanethiol] = 100:5:5, 100:12:12, or 100:21:21, initiator concentration 0.02 mol l^{-1}, temperature 80°C, the synthesis duration 5.5 h.

Prior to the preparation of branched fullerene-containing poly(methyl methacrylate) a solution of C_{60} in toluene was prepared (0.7 g l^{-1}). To ensure complete dissolution of fullerene in toluene the mixture was kept at 5°C for several days. Then a mixture of reagents was added in the molar ratio [monomer **I**]:[monomer **II** or **III**]:[1-decanethiol] = 100:5:5, 100:12:12 or 100:21:21, and copolymerization was carried out under conditions usual for the copolymers.

After completing the polymerization the reaction mixture was cooled and poured to a 10-fold excess of precipitant hexane. The precipitate (fraction 1) was filtered off, washed with hexane, dried in air and in a vacuum at 20°C to constant weight. From the filtrate after evaporation of hexane fraction 2 of the copolymer was isolated. Fractions 1 consisted of amorphous powders, fractions 2 were a highly viscous fluid, those containing fullerene were of brown color.

The kinetics of (co)polymerization of monomer **I** in toluene in the absence and presence of the fullerene was studied by precise isothermal calorimetry on a DAK-1-1 device at 60°C. Conversion *C* of C=C bonds and the reduced rate of (co)polymerization $w/[M]$ were calculated by the known method [13], taking into account the molar heat of polymerization of the monomer **I** in the bulk of 58.8 kJ mol^{-1}.

The content of the C=C bonds in the copolymers were determined by ozonolysis using analyzer of double bonds ADS-4M, with the copolymer solutions in $CHCl_3$, reference stilbene. Absorption curves of ozone by the copolymer solution were recorded and the content of double bonds was calculated by the method of [14].

The molecular weight of the obtained copolymers measured by gel permeation chromatography using a liquid chromatograph Waters GPCV 2000 (two columns of PL-gel, 5 μm, MIXED-C, 300×7.5 mm), equipped with a refractometric detector and light scattering detector WYATT DAWN HELEOS II (λ = 658 nm), eluent THF, temperature 35°C, elution rate 1 ml min^{-1}. The absolute molecular weights of copolymers were obtained by treating the light scattering detector data using the Astra 5.3 2.20 software. Refractive index increment $dn/dc = 0.06–0.07$ ml g^{-1} To calculate the relative molecular weights were used calibration plots for PS standards and the Empower Pro software.

The intrinsic viscosity of copolymers was determined using a VPZh-2 viscometer with a capillary of 0.56 mm diameter from solutions in toluene at 20°C. Extrapolating the dependence of the viscosity on the (co)polymers concentration to zero we obtained the intrinsic viscosity; the slope of the dependence of intrinsic viscosity on polymer concentration in solution was measured. Then, using the Huggins equation $\eta_{\text{reduced}} = [\eta] + k'[\eta]^2c$ and obtained $[\eta]$ values we determined the Huggins constant k', which characterizes the interaction of macromolecules with the solvent.

The glass transition temperature of copolymers (T_g) was determined using a differential scanning calorimeter Mettler Toledo with a heating rate of 5 deg min^{-1}. Glass transition temperatures were measured during the second or third heating-cooling cycles from 0 to 150°C.

Electron absorption spectra of the copolymers in chloroform were recorded with a spectrophotometer Specord M40, the cell thickness 0.5–1 cm.

The IR spectra of the copolymer films cast from chloroform were recorded on a Specord M80 spectrophotometer. The IR spectra of viscous samples were taken between the KBr glass.

The ESR spectra of fullerene in the course of (co)polymerization were recorded at room temperature using a RE-1306 radio spectrometer (working frequency 9.4 GHz) coupled with a computer through the ADC to obtain spectra in digital form. The concentration of the fullerene radical was determined by double integration of the source ESR spectrum and by comparison with the reference with a known content of paramagnetic sites.

The thermogravimetry investigations were carried out on electronic thermal balance ATV-14M [15] at a linear heating rate 4 deg min^{-1} in an atmosphere of dry argon.

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