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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Thermal Degradation of a Heteroarm Starlike Polymer with Fullerene C^{60} Core

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Abstract—The mechanism of thermal degradation of a 12-arm starlike polymer with fullerene C_{60} core and equal number of polystyrene and poly(*tert*-butyl methacrylate) arms was studied by thermal desorption mass spectrometry. Thermal characteristics of the heteroarm stars were compared with those of six-arm starlike fullerene-containing polystyrenes and linear poly(*tert*-butyl methacrylate).

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Fullerene(C_{60})-containing polymers and composites attract steady researchers' interest, because these materials exhibit a unique combination of physicochemical properties [1, 2]. Among fullerene-containing polymers, of particular interest are starlike polymers in which arms of different nature are covalently linked to a common C_{60} core. Such polymers are of considerable scientific and practical interest owing to smart polymer properties [3, 4]. They are used as micelle-forming agents [5, 6], as nanocontainers and nanoreactors [7], and for preparing gas-separating membranes and films with a highly ordered morphology [8, 9].

Previously we studied the thermal properties of both mixed polymer/fullerene systems (composites) and polymers containing covalently bound fullerene C_{60} [10–16]. We showed that the decisive factor of their heat resistance is the extent of the fullerene dispersion in the polymer matrix (molecular and/or cluster dispersion). For polymers containing fullerene in the covalently bound state, of major importance is the stability of chemical bonds between fullerene C_{60} and polymer chain. In particular, in the above-mentioned papers we reported data on the heat resistance of starlike polystyrenes (PSs) with the C_{60} core, described by the formula $(PS)_nC_{60}$, where the number n of grafted PS chains is 2, 4, or 6.

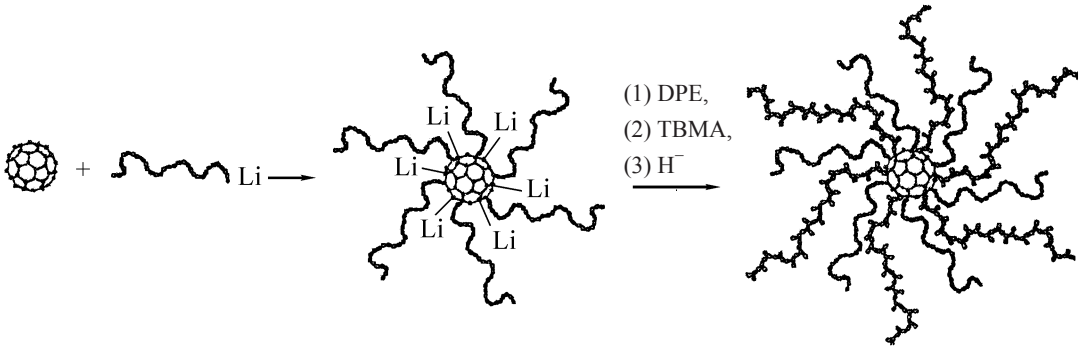
In this study we examined thermal degradation of a polymer of a more complex architecture: a heteroarm starlike polymer with six PS chains and six poly(*tert*-butyl methacrylate) (PTBMA) chains linked to the C_{60} core. This is the first study of the thermal degradation of a polymer with such type of the structure. It seemed important to study the heat resistance of heteroarm starlike polymers in which arms of polymers of different chemical nature are linked to a common core and to compare the thermal properties of such polymers with those of starlike homopolymers consisting of six PS chains grafted to fullerene C_{60} [11, 14].

Particular attention was given to obtaining additional data on the heat resistance of PTBMA homopolymer after subjecting it to a weak mechanical action. Such treatment of the polymer may give rise to new unstable bonds, which will lead to changes in the mechanism of thermal degradation. A study of the mechanically modified polymer allowed us to obtain additional information on the degradation products and mechanisms of their formation, and also to compare the character of PTBMA thermal degradation with data both for the initial polymer (without mechanical treatment) and for PTBMA arms in the starlike hybrid polymer $(PS)_6C_{60}(PTBMA)_6$.

EXPERIMENTAL

The starlike heteroarm polymer $(PS)_6C_{60}(PTBMA)_6$ containing six PS arms and six PTBMA arms was

Scheme 1.



prepared via the step of formation of six-arm starlike PS [17] with active centers C_{60}–Li, $(PS)_6C_{60}Li_6$, followed by modification of the active centers with 1,1-diphenylethylene (DPE). The modified starlike PS (macroinitiator) was used for initiating anionic polymerization of polar TBMA monomer in accordance with the Scheme 1.

According to sedimentation–diffusion analysis and viscometry, the polymer $(PS)_6C_{60}(PTBMA)_6$ had a regular starlike structure, with the molecular weight $M_{SD} = (48 \pm 8) \times 10^3$ [17]. The molecular weights $M_{\underline{n}}$ of the arms, determined by exclusion chromatography, were 3.7×10^3 for PS arm and 4×10^3 for PTBMA arm.

PTBMA homopolymer with $M_n = 10.9 \times 10^3$ and $M_w/M_n = 1.04$ was prepared by anionic polymerization of the corresponding monomer in THF with an adduct of oligostyryllithium with DPE used as initiator, following the procedure described in [18].

The mass spectrum of TBMA (98%, Aldrich) was taken on an MSKh-6 mass reflectron (Sumy, Ukraine) in the mode of dosed admission of monomer vapor into the mass analyzer at room temperature. The standard ionizing electron energy was 70 eV.

The kinetics of fullerene C_{60} desorption was monitored by the temperature dependence of the intensity of the molecular ion C_{60}^+ (m/z = 720).

Thin films of PTBMA homopolymers and the hybrid polymer $(PS)_6C_{60}(PTBMA)_6$ were prepared by applying a 0.1 wt % toluene solution of a polymer on a support-heater (200-μm thick stainless steel foil) equipped with a thermocouple, using a chromatographic microsyringe. The film was dried in air for 10 min. The thickness of the dry film was estimated from the solution volume, polymer density, its concentration, and area occupied by the applied drop. The film thickness did not exceed 100 nm, which allowed rapid heating of the sample in thermal degradation experiments.

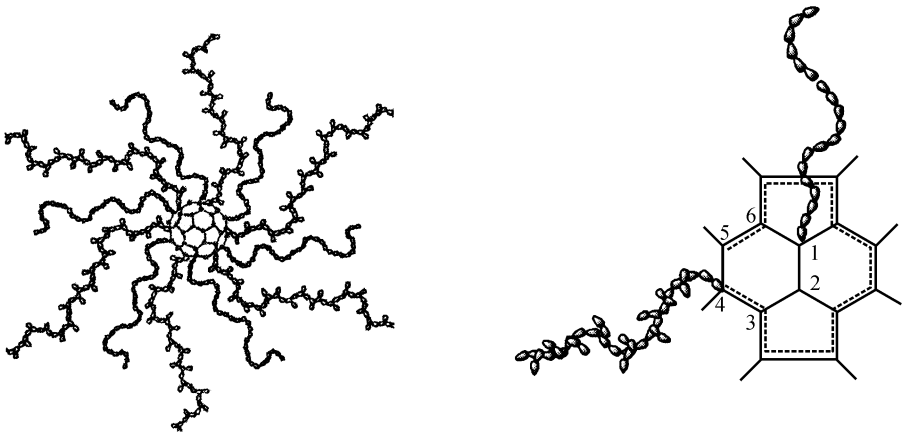
The mass spectra of volatile products of thermal degradation of the polymers were taken with an MSKh-6 mass reflectron with an improved high-vacuum attachment for thermal degradation. The device was equipped with a new unit for recording mass spectrum, which allowed simultaneous computer recording of the kinetics of the intensity variation for any ten selected peaks of the spectrum, of the sample temperature, and of the pressure in the device chamber [19]. The vacuum in the system was kept at a level of 5×10^{-5} Pa. The polymer films were heated at a rate of 7 deg s^{-1}.

The macromolecule of the heteroarm polymer $(PS)_6C_{60}(PTBMA)_6$ has a starlike structure, with six PS arms and six PTBMA arms grafted to a common C_{60} core [17]. In pyracylene fragments of the fullerene core, the arms are linked in (1,4) positions [20] (Scheme 2).

The starlike structure, hybrid composition of the macromolecules, and presence of covalent bonds C_{60}–polymer chain suggested more complex character of thermal degradation of these materials compared to the related processes involving linear homopolymers. For reliable identification of volatiles released in the course of degradation of such complex polymers, it was necessary to have information on specific features of thermal degradation of each type of the polymer incorporated in hybrid macromolecules. The mechanism of thermal degradation of PS is well known [21]. On the contrary, specific features of thermal degradation of PTBMA have been studied in insufficient detail, and therefore we additionally examined the heat resistance of PTBMA.

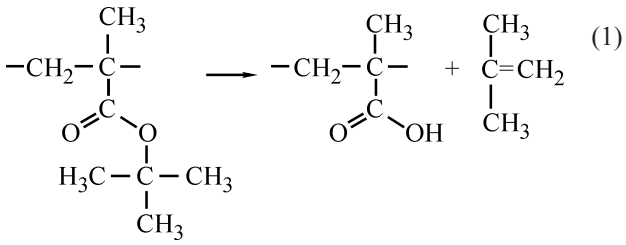
The experimental procedure of thermal desorption mass spectrometry that we used combined the mass spectrometric and thermal desorption techniques and allowed us to monitor the sequence of elementary events

Scheme 2.



in a complex process of degradation of the polymeric material. The procedure appeared to be particularly efficient in studying thin polymer films applied onto a substrate from solutions.

Thermal degradation of poly(*tert*-butyl methacrylate). Thermal degradation of poly(alkyl methacrylates) follows the depolymerization pathway, with separation of monomer molecules from the end of a free macroradical formed by homolysis of the C–C bond in the backbone. However, this process is sometimes complicated by decomposition of pendant groups of the macromolecule and other reactions [21]. Their competition can be noticeably manifested in more complex processes, e.g., in the course of tribological, thermomechanical, and other tests of the polymeric material. Thermal degradation of PTBMA is accompanied by elimination of isobutylene [21], with transformation of PTBMA into polymethacrylic acid:



(1)

It is known that the actual mechanism of thermal degradation of a polymer depends on the procedure of its synthesis (polymerization method). Therefore, we examined the PTBMA homopolymer prepared by anionic polymerization. The potential of the mass spectrometric device we used allowed simultaneous recording of all peaks of products released in the course of heating of a PTBMA film. The mass spectrum of volatile products in the initial step of the thermal degradation of PTBMA contains six major peaks (in the order of decreasing intensity), *m/z* (I_{rel}, %): 41 (100), 39 (85), 56 (45), 28 (22), 27 (22), 55 (16). This set of peaks should be assigned to the release of isobutylene (IB) [22], which undergoes fragmentation under electron impact. Therefore, any of these peaks reflects the temperature dependence of the rate of IB formation to the same extent. It can be seen from the temperature dependence of the rate of IB release in the course of heating a PTBMA film (Fig. 1) that the thermal degradation starts at a temperature close to 230°C. For simplicity sake, we show in Fig. 1 only one curve related to the molecular ion (*m/z* 56). The rate of IB release from the film reaches a maximum at 300°C, after which the thermal degradation rate decreases. Thus, in the examined temperature interval the mechanism of thermal degradation of PTBMA is determined by elimination of an

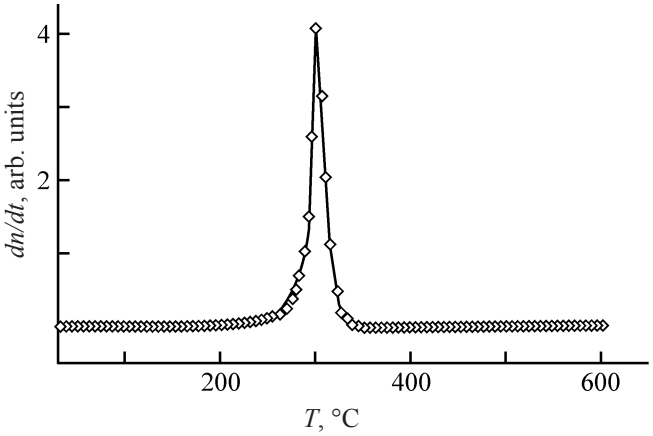


Fig. 1. Temperature dependence of the rate of IB release *dn/dt* in the course of PTBMA heating.

IB molecule from the pendant ester group of the polymer chain [scheme (1)].

Heat resistance of PTBMA after mechanical action. In the heteroarom starlike polymer $(PS)_6C_{60}(PTBMA)_6$, there are two types of bonds of C_{60} with PTBMA and PS arms. It should be expected that the character and energy of these bonds should affect the mechanism of thermal degradation of polymer arms of different nature. To obtain additional information on these processes, it was appropriate first to study possible changes in the mechanism of thermal degradation of PTBMA after subjecting it to a weak mechanical action. We expected that cleavage of C–C bonds in the backbone and subsequent radical processes in PTBMA would give rise to new weak bonds initiating depolymerization under thermal action. The polymer was subjected to short manual grinding in an agate mortar.

For mechanically modified PTBMA, we monitored all the peaks of degradation products in the mass spectra (see table). It can be seen that the mass spectrum of modified PTBMA differs from that obtained for the untreated (initial) PTBMA. We assumed that all the recorded peaks were due to formation of TBMA monomer in the course of depolymerization. To confirm this hypothesis, we examined the mass spectrum of pure TBMA monomer (Fig. 2) in the mode of dosed admission of its vapor into a mass analyzer at room temperature, because in the available catalogs we have not found the mass spectrum of this compound. The spectrum of the monomer (Fig. 2)

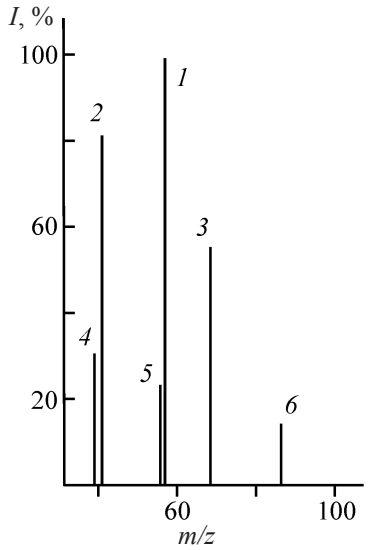


Fig. 2. Mass spectrum of TBMA monomer: (*I*) relative intensity and (*m/z*) weight-to-charge ratio of ions. Fragment ions, *m/z*: (*1*) 57, (*2*) 41, (*3*) 69, (*4*) 39, (*5*) 56, and (*6*) 87.

Products of thermal degradation of PTBMA after its mechanical modification

Fragment ion	t g^{-1}	Relative intensity of peak, %
$C_4H_9^+$	57	100
$C_3H_5^+$	41	85
$C_4H_5O^+$	69	62
$C_3H_3^+$	39	51
$C_4H_8^+$	56	18
$C_4H_7O^+$	87	15

appeared to fully coincide with the set of fragment ions recorded in the course of heating of mechanically treated PTBMA.

It should also be noted that the mass spectrum of the monomer does not contain a peak of TBMA molecular ion (*m/z* 142). The same is true for all the other butyl methacrylate isomers subjected to electron impact. The release of the monomer, detected by the fragment peak with *m/z* 57 on heating the sample subjected to mechanical treatment (Fig. 3), occurs in two steps in the temperature intervals 60–150°C with T_{max} = 130°C and 150–220°C with T_{max} = 185°C. As seen from these data, the degradation starts at considerably lower temperatures than in the case of unmodified PTBMA, which is indicative of formation of unstable bonds in the polymer chains.

It is known [23–26] that the activation energy E_a of depolymerization of structurally related poly(methyl methacrylate) (PMMA), measured in the temperature interval 60–160°C, is about 74 kJ mol^{-1}. For the low-temperature step of thermal degradation of the examined PTBMA sample, E_a is approximately 90 kJ mol^{-1} (for

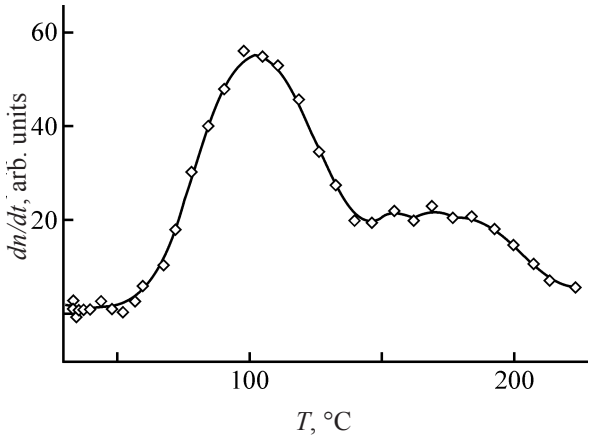


Fig. 3. Temperature dependence of the rate *dn/dt* of the release of TBMA monomer in the course of heating mechanically treated PTBMA.

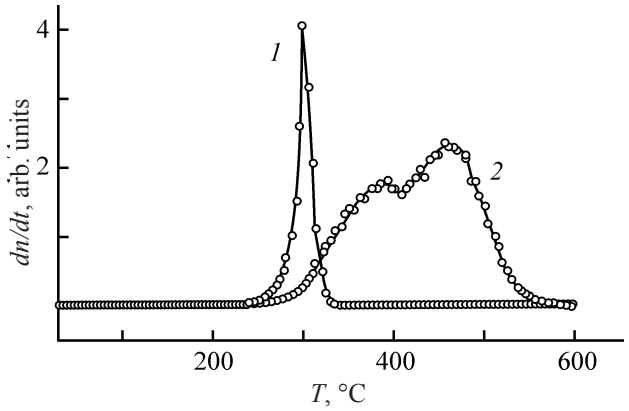


Fig. 4. Temperature dependence of the rate *dn/dt* of the release of volatile products in the course of heating a film of heteroarm starlike polymer $(PS)_6C_{60}(PTBMA)_6$. Release of (*1*) isobutylene and (*2*) styrene.

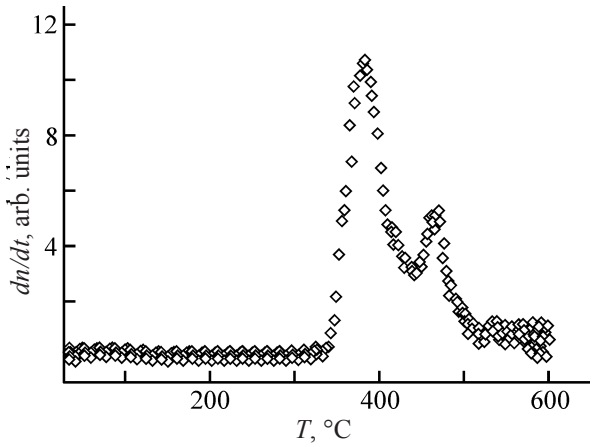
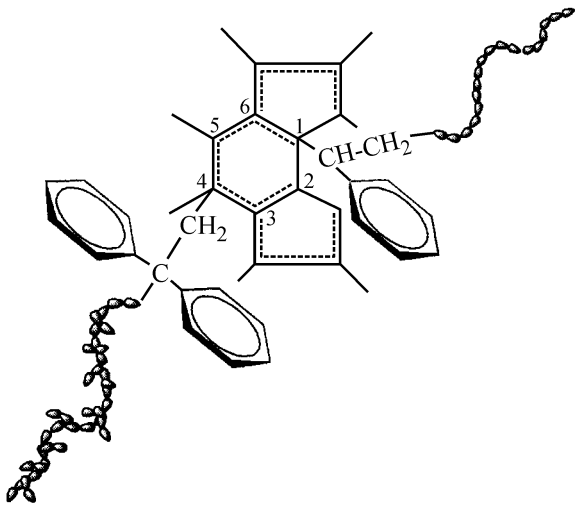


Fig. 5. Temperature dependence of the rate *dn/dt* of the release of fullerene C_{60} in the course of heating a film of the heteroarm starlike polymer.

Scheme 3.



calculation details, see [27]). Comparable values of the activation energy for PMMA and PTBMA suggest that the main mechanism of thermal degradation of mechanically treated PTBMA is depolymerization.

Thermal degradation of the heteroarm polymer $(PS)_6C_{60}(PTBMA)_6$. The release of volatile products in the course of thermal degradation of $(PS)_6C_{60}(PTBMA)_6$ starts at ~230°C (Fig. 4). The rate of IB formation (monitored by any of fragment ions) reaches a maximum at T_{max} = 300°C (Fig. 4, curve *1*), i.e., under the same conditions as on heating mechanically untreated PTBMA (Fig. 1). The results obtained indicate that PTBMA arms in the heteroarm polymer do not contain bonds that are significantly less stable than the C–O bonds in the linear (untreated) PTBMA homopolymer.

Curve *2* in the thermogram (Fig. 4) refers to the release of styrene (*m/z* 104) in thermal degradation of PS arms in the hybrid starlike polymer. Styrene is formed in two steps. Intense release of the monomer occurs at T_{max} = 380 ± 10 and 470 ± 10°C. Similar bimodal pattern was observed previously [11, 14–16] in studying thermal degradation of starlike six-arm polymers $(PS)_6C_{60}$. The presence of two peaks in the thermogram was attributed to depolymerization initiation by cleavage of two types of covalent bonds. The first peak was assigned to cleavage of the weakest bonds between the fullerene core and the PS chain. The monomer release rate was maximal at T_{max} = 360°C. The second, high-temperature step of the styrene release was attributed to cleavage of C–C bonds in PS chains after their detachment from the C_{60} core [15, 16].

For the high-temperature step in the thermogram (Fig. 4) corresponds T_{max} ~450°C. Presumably, thermal degradation of PS chains in the hybrid polymer $(PS)_6C_{60}(PTBMA)_6$ occurs in the same manner as in the six-arm PS, $(PS)_6C_{60}$. The dissociation energy of bonds between the C_{60} core and the polymer chain apparently depends on the nature of this bond and position of the chain in the pyracylene fragment of the C_{60} molecule [1 or 4 (Scheme 3).

The PS chain occurs in position 1 and is linked to the C_{60} core via carbon atom bonded to the phenyl ring of the PS monomeric unit. In accordance with published data [28], the dissociation energy of the C–C bonds in the β-position relative to the terminal C=C bond in the backbone is 40 kJ mol^{-1} lower than that of the C–C bond in the backbone. In the heteroarm polymer, the C_{60}–PS bond is in the β-position both to the C=C bond of the

phenyl ring of the PS chain unit and to the C=C bond in the pyracylene fragment of the C_{60} molecule, and therefore its dissociation energy should be lower than that of the C–C bond in the PS backbone.

PTBMA arms are linked to the C_{60} core in position 4 through the $–CH_2C(Ph)_2–$ group [17, 20]. Therefore, the first bond between the C_{60} core and the PTBMA chain is the $C_{60}–CH_2$ bond whose strength is apparently close to that of the C–C bond in the backbone. This fact explains why no release of volatile products corresponding to cleavage of bonds that are weaker than C–O bonds in pendant ester groups of PTBMA is observed in the low-temperature step (<200°C) of thermal degradation of the hybrid polymer. The results we obtained are consistent with the concept that the bond between the fullerene core and PTBMA chain is stronger than the C_{60}–PS bond.

Release of fullerene C_{60} from the heteroarm polymer. Figure 5 shows the temperature dependence of the rate of fullerene release from a film of the 12-arm hybrid polymer. Two maxima at 380 and 470°C are observed. As C_{60} can be released only on complete elimination of all the arms from the fullerene molecule, the presence of the second maximum is yet unclear, and further studies are required to account for this phenomenon. The character of C_{60} release can depend on thermodynamic and kinetic features of elimination of different chains from the fullerene core in macromolecules. Complex pattern of fullerene release was observed previously in studying thermal degradation of starlike polystyrenes with different numbers of arms [14].

CONCLUSIONS

(1) Specific features of thermal degradation of a heteroarm starlike polymer containing arms of different chemical nature (polar and nonpolar) on a common core, fullerene C_{60}, were studied.

(2) Degradation of polystyrene arms in starlike heteroarm polymers and six-arm homopolystyrenes occurs by a common two-step depolymerization mechanism via cleavage of two types of bonds: weak covalent bonds between the C_{60} core and polystyrene chain and stronger C–C bonds in the backbone.

(3) Thermal degradation of arms of the polar polymer is similar in the mechanism to that of poly(*tert*-butyl methacrylate) containing no defective (weak) bonds in the backbone.

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