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Low-temperature postradiation quasi-living radical polymerization of acrylic monomers in the presence of fullerene C_{60}

Viktoriya A. Pakhomova, Dilyara A. Gordon, Alexander I. Bol'shakov and Alfa I. Mikhaylov*

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 496 515 5420; e-mail: alfaim@icp.ac.ru

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Water-soluble fullerene C_{60}-containing polymers of acrylamide and acrylic acid were obtained by low-temperature radiation-induced quasi-living radical polymerization.

The modification and functionalization of nanomaterials to obtain water-soluble derivatives is of interest in medicine and biology.[1] We have investigated low-temperature γ-induced postpolymerization of acrylic monomers such as acrylamide (AA) and acrylic acid (AAcid) in the presence of fullerene C_{60} using optical and EPR spectroscopy and calorimetry. The radiation initiation has an advantage because it does not require inclusion of the substantial initiators or catalysts.

In this work, C_{60} of 99.5% purity was used. For a more homogeneous distribution of acting molecules, the solution of the C_{60} in toluene was prepared (1–1.5 mg of C_{60} per 1 ml of toluene), which was mixed with 15% solutions of vinyl monomers in ethanol (1:4 for AAcid and 1:2 for AA). A sample prepared in such a manner was evacuated and irradiated at 77 K at 40–50 kGy. After that, the sample was heated gradually at a rate of 10 K h^{-1}.

The polymerization of acrylic and other monomers in a viscous matrix of ethanol has been investigated previously.[2,3] It has been shown that the initiation of polymerization and a further growth of the polymer chain took place after the transition from a glassy state to a viscous overcooled liquid. Propagating polymer chains being able to grow quickly turned out to be stable under the conditions of overcooled liquid, *i.e.*, the macroradicals R_p do not terminate. Therefore, the polymerization occurred according to the mechanism of quasi-living (without termination) radical polymerization. To investigate how fullerene affects the polymerization of AA and AAcid in a highly viscous matrix of ethanol, the low-temperature polymerization of these monomers in the presence of fullerene was carried out under identical conditions. In Figure 1, calorimetric curves of heating of a cooled (77 K) mixture of a 15% AA solution in ethanol and fullerene in toluene (1 mg cm^{-3}) before (1) and after (2) γ-irradiation at 77 K are given. At 110–115 K, the transition from a glassy state to an overcooled liquid took place. In Figure 1(*b*) one can see a decay of radicals obtained during irradiation. The EPR spectra were recorded on an EPR-21 spectrometer ($\lambda = 3.2$ cm) at a microwave power of about 10^{-4} W. In Figure 1(*c*) one can see simultaneous transformation of EPR spectra caused by polymerization starting, completed at 120 K, when only propagating polymer radicals R_p exist in the system. Upon further heating, the heat evolution due to polymerization can be seen in calorimetric curves [Figure 1(*a*)]. In the temperature range 120–135 K, the concentration of R_p remains constant while polymer chains grow effectively. It is because the mobility of propagating macroradicals is limited to recombine while the mobility of monomer

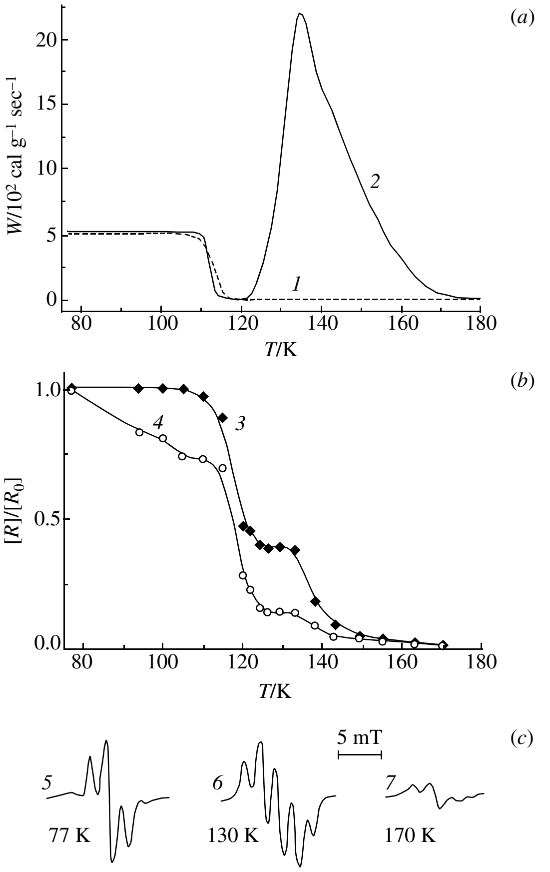

Figure 1 (*a*) Calorimetric curves of a mixture of AA in ethanol (15%) and C_{60} in toluene (1mg cm^{-3}) (*1*) before and (*2*) after γ-irradiation. (*b*) Radical concentration *versus* heating temperature: (*3*) AA in ethanol (15%), (*4*) a mixture of AA in ethanol (15%) and C_{60} in toluene (1 mg cm^{-3}). (*c*) Transformation of the EPR spectra of this irradiated mixture as a function of temperature.

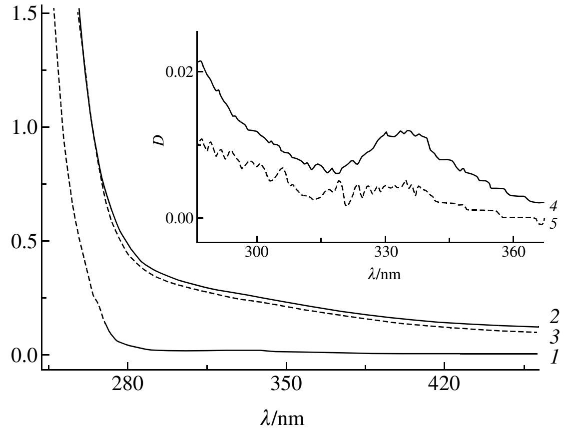

Figure 2 Absorption spectra of aqueous solutions: (*1*) PAA (30 mg cm^{-3}), FPAA (30 mg cm^{-3}) (*2*) before and (*3*) after double extraction with toluene; absorption spectra of the (*4*) first and (*5*) second toluene extracts from FPAA.

molecules is sufficient for reaching active centres to grow the chain. The EPR and calorimetric study of the system where AAcid was used instead of AA showed that the process follows the same rules. Thus, from a comparison of calorimetric and EPR data, one can conclude that the polymerization of vinyl monomers in an ethanol matrix occurs according to a quasi-living radical polymerization mechanism in the presence of fullerene, as well as in the absence of fullerene.[2,3] In this work, we found an effect of fullerene on the decay of radicals [Figure 1(*b*)]. For C_{60}-containing polymers, the concentration of propagating macroradicals is lower ($[R_p] = 0.15[R_0]$, R_0 is the radical of initiation) than that for polymers without fullerene ($[R_p] = 0.4[R_0]$). Actually, the yields of pure AA and AAcid polymers (PAA, PAAcid) obtained under identical conditions are ~98 and 57%, respectively, while the yields of fullerene-containing polymers FPAA and FPAAcid are equal to 72 and 21%, respectively. The reason for the decrease of efficiency may be that after fullerene addition to the macroradical R_p, the latter becomes inactive because of delocalization of unpaired electron in the conjugated system.[4] These results are in a good agreement with published data.[5] However, fullerene almost completely inhibits the polymerization for most vinyl monomers (polymer yields of ~8–10%). In our case, the technique of quasi-living radical polymerization allowed us to produce fullerene-containing polymers in good yields (~70%). The polymers obtained are readily water-soluble. Apart from the transparent yellow liquid portion in a polymer water solution, there is a residue, which cannot be dissolved in traditional solvents such as dimethylformamide. The sediment portion with respect to the total mass of polymer is ~3%. In Figure 2 (spectra *1*–*3*), the absorption spectra of PAA and FPAA are presented. Unlike PAA, FPAA displayed an additional unstructured gradually descended absorption in the region 240–700 nm, characteristic of covalent combined[5,6] fullerene or its associates.[7] In order to separate the strongly covalent-bound C_{60} molecules from weakly (dynamically) bound molecules, double extraction was performed with toluene from an aqueous polymer solution. In Figure 2 (spectra *4* and *5*) the spectra of these extracts are given. In the second extraction spectrum the band at 330 nm, characteristic of free fullerene or its complexes is almost absent. The spectrum *3* (Figure 2) of FPAA, after a double extraction from it of dynamically bound C_{60}, did not show a significant change.

The amount of C_{60}, summarised by taking in consideration all extracts with toluene is 7% for both AA and AAcid polymerization in the presence of fullerene. Thus, 93% of fullerene molecules interacted forming both a fullerene-containing polymer and, possibly, a homopolymer contained in the residue. The C_{60} content of a water-soluble part of the product is ~0.5%.

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