

Brief Communications

Polymerization of [60]fullerene activated with butyllithium

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Fullerene polymerization caused by addition of an alkylating agent was discovered. Alkylation of fullerene with primary or secondary butyllithium gave both mono- and polynuclear products (polyfullerenes). The polymerization rate of the intermediates $\text{Bu}_n\text{C}_{60}\text{Li}_n$ ($n < 6$) is nearly the same as the rate of the addition of BuLi to fullerene. Molecules C_{60} can polymerize as well; however, the rate of this reaction is much lower than the polymerization rate of the reactive intermediate species.

Key words: fullerene, butyllithium, polymerization.

The closed sphere of a [60]fullerene molecule consists of 60 sp^2 -hybridized carbon atoms and tends toward various addition reactions (radical and nucleophilic addition, cycloaddition). Quantum-chemical calculations¹ and numerous experiments have revealed that six out of 30 double bonds are most reactive. It is these double bonds that are involved first in any addition reaction, in particular, polymerization.

Fullerene polymerization under drastic conditions of "physical" experiments (solid state, high temperature and high pressure, various kinds of irradiation, *etc.*) has already become a classic, being cited in relevant manuals.² The formation of stable fullerene polymers consisting entirely of carbon atoms involves a [2+2] cycloaddition reaction in which adjacent molecules form a cyclobutane structure between them through opening of their two double bonds. Data on fullerene polymerization under mild "chemical" conditions (relatively dilute solutions, moder-

ate temperatures, and moderate pressure) are scarce. The formation of dimers has been observed² in the synthesis of some fullerene derivatives. In these cases, the cages C_{60} are linked by single carbon-carbon bonds. It is known that homopolymerization of C_{60} in solution can be initiated by benzoyloxy³ and cyanoisopropyl radicals.⁴ However, no polymerization (or at least dimerization) of fullerene in the presence of organolithium compounds has been mentioned in the literature.

Nucleophilic addition of organometallic compounds (in particular, BuLi) to fullerene has been known for 20 years^{5,6} and is considered to be useful for its alkylation. The addition occurs very rapidly. With toluene as a solvent, addition of BuLi immediately results in the precipitation of salt $\text{R}_n\text{C}_{60}\text{Li}_n$ ($n \leq 6$). Replacement of the lithium atom by hydrogen (*e.g.*, by adding methanol to the reaction mixture) leads to toluene-soluble alkyl derivatives of C_{60} .

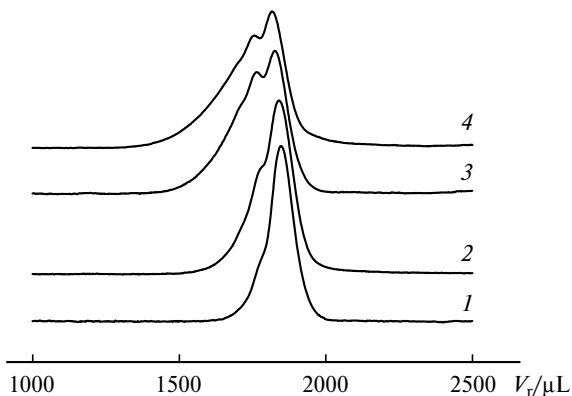


Fig. 1. GPC data of C_{60} derivatives: toluene-soluble (1) and toluene-insoluble PHAF (2) prepared from Bu^sLi , (3) PHAF prepared from Bu^nLi , and (4) alkylated fullerene $(Bu^nLi)_n C_{60}H_n$; V_r is the retention volume.

Earlier,⁷ we have developed a method for the synthesis of polyhydroxylated fullerene of the general formula $Bu_n C_{60}(C_2H_4OH)_n$ named poly(hydroxyalkyl)fullerene (PHAF). The first step involves addition of primary (Bu^nLi) or secondary butyllithium (Bu^sLi) to C_{60} . To introduce fragments $-C_2H_4OH$, the lithium atoms are replaced by ethylene oxide followed by deactivation of the group OLi with methanol. The products isolated from the reaction mixture (the yield with respect to fullerene is 100%) are finely divided dark brown powders that are soluble, as distinct from C_{60} , in most organic solvents. Like other researchers, at that time we did not assume that alkylation products could include fullerene polymers. That is why the results obtained by gel permeation chromatography (GPC) for the reaction products were absolutely unexpected: the shape of GPC curves suggested that the mixture contains oligomeric products with different degrees of polymerization (Fig. 1).

The goal of this study was to specify the reaction step at which polymer structures form and the reactive species that participate in polymerization, as well as to estimate the sizes of the resulting oligomers.

Experimental

The procedure for the synthesis of fullerene derivatives in toluene and selected characteristics of the products obtained were described earlier.⁷ GPC data were recorded on a Millikrom chromatograph coupled with a UV detector. Silanized silica gel (LiChrospher 100 S) was used as a stationary phase (column 20×0.4 cm, THF as an eluent). Preparative GPC was carried out on a Waters 200 chromatograph (three Styragel columns 200, 500, and 1000 Å, 125×0.9 cm) coupled with a refractometer (THF as an eluent).

In a chromatographic column operated in the GPC mode, entering molecules are separated by size. Earlier,⁸ it has been shown that the van der Waals molecular volume V is the versatile characteristic of a molecule's size in GPC. The volume V is cal-

culated from the volume increments of the constituent atoms of the molecule.⁹ This substantially simplifies the calibration of a column. The calibration consists in determining the eluent volume V_r corresponding to a peak on the GPC chromatogram of a known compound and plotting $\ln V$ versus V_r . For analysis of samples of fullerene derivatives, we calibrated the column against individual aromatic compounds. The equation for the calibration straight line (V_r is quoted in μL , V is quoted in \AA^3) has the form:

$$\ln V = 36.7628 - 0.0161 V_r. \quad (1)$$

The UV spectra of C_{60} and deactivated products of its reaction with $BuLi$ were recorded on a Specord M-40 spectrophotometer in the 290–700 nm range. In the spectrum of C_{60} in toluene, this range contains an intense absorption band from 315 to 450 nm, with a peak intensity at 330 nm. The spectrum of products obtained by polyaddition of various groups to C_{60} represents a smooth descending curve tending to nearly zero absorption at 700 nm.

Results and Discussion

The GPC curves of a PHAF sample (see Fig. 1, curve 2) and its fractions obtained by preparative GPC are shown in Fig. 2. The vertical lines correspond to the V_r values calculated by Eq. (1) for oligomers of different degrees of polymerization. The molecular volumes of oligomers V were calculated under the assumption that the cages C_{60} are linked by single carbon–carbon bonds and that all 12 reactive carbon atoms are involved in the addition of the cages C_{60} and the Bu and HOC_2H_4 groups. It can be seen that the sample contains not only mono-, bi-, and trinuclear products but also oligomers with substantially higher degrees of polymerization.

It was interesting to find out which species participate in polymerization. The alkylation reaction of fullerene characterized by that even monolithiumalkylated fullerene (the number of $BuLi$ molecules added to C_{60} may be up to six) is an insoluble salt causes the coprecipitation of unre-

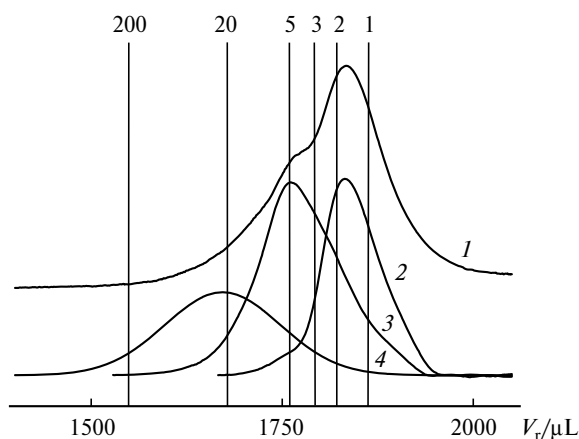


Fig. 2. GPC data of PHAF (1) and its fractions (2–4). The upper line indicates the number of monomer units in the oligomers.

acted C_{60} molecules.⁵ Therefore, one could assume that polymerization would involve both C_{60} molecules and their butyllithium derivatives (intermediates). To verify this assumption, we carried out alkylation of C_{60} for a molar $Bu^sLi : C_{60}$ ratio of 2 (*i.e.*, the amount of BuLi in solution is much fewer than fullerene can add). The reaction mixture was periodically sampled; the samples were deactivated with methanol and examined by UV spectroscopy. Before the addition of BuLi (0 min), the spectrum of the solution is obviously the spectrum of C_{60} in toluene. The spectra of all the other samples (the reaction time was varied from 5 min to 6 days) are virtually identical: the smooth descending curve characteristic of polysubstituted C_{60} shows a band at 330 nm. This implies that fullerene, which did not react with BuLi within first minutes (or even seconds) of the reaction because of the deficiency of the latter, remains intact for a prolonged period of time. If some more BuLi is added to the reaction mixture left for six days, the spectrum of a sample withdrawn 5 min after the addition of BuLi no longer contains the band at 330 nm. This indicates that the nonconsumed C_{60} completely reacted with BuLi.

When analyzing the GPC data of the products isolated from the withdrawn samples, we obtained an unexpected result. Figure 3 displays the GPC curves of the starting fullerene C_{60} (1) and its alkylation products 5 min (2), three days (3), and six days (4) after the beginning of the reaction (4). It can be seen that the reaction immediately produces oligomers. Therefore, the addition of BuLi to C_{60} is accompanied by polymerization of the intermediates $Bu_nC_{60}Li_n$ ($n < 6$). Chromatograms 2 and 3 are identical (see Fig. 3); this suggests that the molecular composition of oligomeric products formed after 5 min has remained nearly the same for three days. After six days, the peaks corresponding to the higher-weight-molecular oligomers show a relative increase. Apparently, C_{60} molecules can also add to the oligomers of the intermediates; however, the rate of this process is much lower than the polymerization rate of reactive intermediate species. It should be noted that oligomeric products were obtained not only at a low concentration of BuLi in the reaction mixture but also at its high (10–20-fold) molar excess with respect to C_{60} .

To sum up, the results obtained suggest that the addition of BuLi to fullerene makes the latter more reactive in polymerization. Quantum chemical calculations show¹⁰ that two C_{60} molecules do not dimerize unless they receive additional energy from the outside to overcome the energy barrier. Because the aforementioned "physical" experiments require drastic conditions, this barrier is sufficiently high. Only under such conditions can the resulting fullerene polymers consist entirely of carbon atoms.

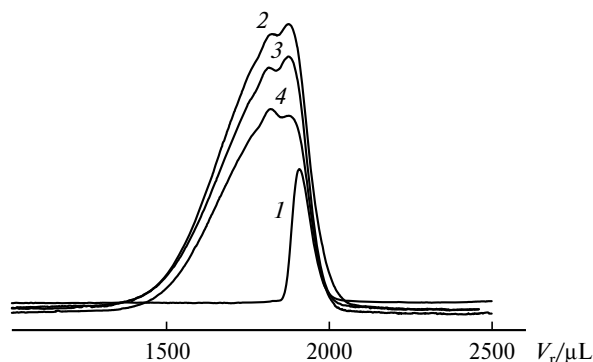


Fig. 3. GPC data of C_{60} (1) and its alkylation products 5 min (2), 3 days (3), and 6 days (4) after the beginning of the reaction.

Under mild conditions of "chemical" experiments, C_{60} molecules seem to be activated by the added fragments of organic (in our case, organometallic) molecules. This is evident from both the previously noticed formation of dimers and polymers in the synthesis of some C_{60} derivatives and the results of this study.

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