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Recent advances in fullerene-based polymers

Ripudaman Malhotra, Sanjiv Mehrotra, Asutosh Nigam

Molecular Physics Laboratory, SRI International,
333 Ravenswood Avenue, Menlo Park, CA 94025, USA

Fullerenes have been incorporated in polymers in several different ways. They have been used as electronegative dopants in poly(aniline) and related materials to produce electrically conducting and photoconducting polymers. Additionally, materials in which the fullerene moieties are chemically bonded to the polymers have also been produced. In these polymers, the fullerene units can either be pendent to a polymer chain, or they can be an integral part of the polymer chain.

We have synthesized an adduct of [60]fullerene with 2-methylaziridine, and prepared many crosslinked polymers by treating this adduct with phenolic and epoxy resins. In general, introduction of the fullerene leads to enhanced thermal stability. The polymers prepared with Novolac also displayed a low coefficient of friction and high resistance to wear. These properties bode well for their use as solid lubricants.

We have also studied the effect of [60]fullerene on AIBN-initiated radical polymerization of a range of vinyl monomers. We found that copolymers were formed with only 2-cyanoethyl acrylate and cyanovinyl acetate whereas in all of the other cases tested, the [60]fullerenes almost completely inhibited the polymerization.

The synthesis and isolation of macroscopic quantities of [60]fullerene has stimulated great interest in fullerene polymers. Along with the development of its chemistry, several different polymers incorporating [60]fullerene have been reported. The first category includes C_{60} doped into polymers.[1,2] Structures in which C_{60} has been chemically bonded into a polymeric network have also been reported. Amato et al. [3] have reported that polymers of C_{60} could be of two different structural kinds: (i) pearl necklace, in which the C_{60} unit is a part of the polymer chain; and (ii) charm bracelet, in which the fullerene unit is pendent to the polymer chain. Later, Taylor and Walton[4] have proposed a lattice-type polymer, which is a two- or three-dimensional variant of the pearl necklace polymers.

We have worked on two different studies on fullerene polymers. The first is the synthesis of an adduct of 2-methylaziridine and C_{60} and preparation of lattice-type polymers from it via ring-opening polymerization.[5] The second is a study on effect of C_{60} on the radical polymerization of styrene.

Polymers from Aziridine Adducts of C_{60}

Prompted by the work of Wudl and coworkers showing the facile addition of amines to C_{60}, we investigated the addition of 2-methylaziridine to C_{60}. Our motivation behind this study was the recognition that aziridine moieties would allow incorporation of the C_{60} cage into a variety of polymers. Typically the adduct was synthesized by stirring C_{60} in dry benzene with an excess of freshly distilled 2-methylaziridine for several days.

Based on the finding that the nucleophilic addition of alkyl amines to C_{60} is hastened at low temperatures we recently developed a rapid procedure for the synthesis of the adduct of C_{60} and 2- methylaziridine.[6] The new procedure calls for freezing the benzene (or toluene) solution of C_{60} and 2-methylaziridine in liquid nitrogen, and thawing the resulting glass. This simple action, which is over in a about 30 min, results in the formation of the adduct. Repeating the freeze-thaw cycle increases the yield. The final product prepared by this low temperature method had an empirical composition corresponding to the addition of six aziridine units as opposed to ten obtained by the earlier method (boiling benzene).

As previously reported, the aziridine adduct reacts readily with epoxy and phenolic monomers via aziridine ring opening to produce polymer with good thermal stability.[5] Accordingly, we prepared polymers of the adduct **1** with epoxides like Epon 828 and phenolic compounds like Novolac and Bisphenol A by heat curing them in different ratios. The Vicker hardness of the polymers from crosslinking Epon 828 with the adduct are shown in Table 1. The results indicate that the hardness of polymer sample first increases with the amount of the adduct, but at higher loadings the hardness decreases sharply. Further work is being conducted to understand this curious behavior.

Copolymers of C_{60} with Vinyl Monomers

Literature reports on radical polymerization of vinyl monomers, conducted mostly with styrene or methyl methacrylate, indicate that the yields of polymers formed in the presence of C_{60} are either very low or the reaction was completely inhibited.[7,8] It has been suggested that in the case of styrene free radical becomes trapped on the fullerene and does not propagate but can terminate. Recently, Camp et al. reported on coplymerizing of C_{60} and styrene by using a large excess of the initiator AIBN.[9] According to the authors, the radicals from the initiator make multiple additions to C_{60} ultimately changing its nature sufficiently such that it would not inhibit polymerization.

We conducted a study on AIBN-initiated radical polymerization of a range of vinyl monomers in the presence of C_{60}. The objective of this study was determine how general is the inhibition of radical polymerization by C_{60} and to see if the fullerene-radicals, which do not readily add to methyl methacrylate and styrene, would add to certain reactive monomers. The vinyl monomers tested were styrene, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, 1-vinyl-2-pyrrolidone, 2- cyanoethyl acrylate (CEA), and 1- cyanovinyl acetate (CVA).

In a typical experiment, 60 to 100 equivalents of the vinyl monomer was added to a suspension of C_{60} (50 mg, 0.07 mmol) in dry THF (2 mL) under argon atmosphere, followed by the addition of catalytic amount of AIBN. The reaction mixture was heated under reflux 75°C for 22 hours. The reaction mixture was evaporated and the weight of the residue was taken as the first indication for the formation of a polymer. In control experiments with these monomers without C_{60}, polymer formation in almost quantitative yields was observed. However, in the presence of C_{60}, polymerization in six out of the eight monomers was substantially inhibited (Table 2). The polymer yield in the presence of C_{60} was less than 10% of that in the absence of C_{60} in the case of methyl acrylate and N-vinyl pyrrolidone; it was 12% for vinyl acetate, 15% for acrylonitrile and 17% for styrene. These results are in accord with C_{60} being an effective inhibitor for radical polymerization of these monomers.

The more reactive CEA and CVA monomers underwent facile polymerization in the presence C_{60}. The polymer yields were around 60% of the value obtained in the control experiment. We were concerned that these monomers may be undergoing reaction by a completely different mechanism, for example by anionic polymerization promoted by traces of moisture. Thus, we conducted tests without the AIBN. In these cases, no polymerization was observed. Thus, confirming the radical nature of the polymerization of these two monomers.

The polymers obtained from CEA and CVA in the presence of C_{60} were characterized by UV absorption spectroscopy. The spectra of polymers in the presence of C_{60}showed strong, broad bands in the 300 to 700 nm range. These bands were absent in the materials recovered from the polymerization in the absence of C_{60}. The UV absorption data provided evidence for the covalent incorporation of C_{60} into the polymer, and the product is best described as a copolymer of C_{60} and CEA (or CVA).

Thermal characterization of the polymers showed that the presence of the fullerene did not affect the onset of decomposition, although the char yield was higher with fullerene co-polymers when compared to the homopolymer.

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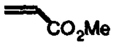
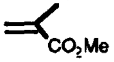
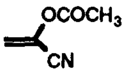
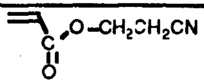
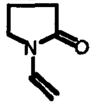
Table 1

Vickers Hardness for Epon 828 Cured with Varying Amounts of the C_{60}–2-Methyl Aziridine Adduct

% Adduct	Vickers Hardnes (kg/mm^2)
0	620
33	800
50	290

Table 2

Effect of [60]fullerene on the yield of polymers from AIBN-initiated polymerization of various vinyl monomers at 65°C.

Monomer	**Structure**	**Polymer Yield (%)**	
		with C_{60}	**Control**
Methyl acrylate		**9**	**97**
Methyl methacrylate		**14**	**98**
Acrylonitrile		**11**	**76**
Cyanovinyl acetate		**53**	**92**
Vinyl acetate		**9**	**75**
2-Cyanoethyl acrylate		**65**	**99**
Styrene		**15**	**85**
N-vinyl pyrrolidone		**8**	**100**