Effect of [60]fullerene on the radical polymerization of alkenes

Sanjiv Mehrotra, Asutosh Nigam and Ripudaman Malhotra*

Chemistry and Chemical Engineering Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA

AIBN-initiated radical polymerization of 2-cyanoethyl acrylate and cyanovinyl acetate in the presence of [60]fullerene produces copolymers in good yields, whereas for most other vinyl monomers [60]fullerene almost completely inhibits 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 consisting of covalently linked fullerenes and copolymers in which fullerenes are a part of the polymer backbone.[1] In all previous reports on radical polymerization of vinyl monomers, conducted mostly with styrene or methyl methacrylate, the yields of polymers formed in solution were either very low or the reaction was completely inhibited.[2,3] It has been suggested that in the case of styrene, the free radicals are trapped by fullerene, and the resulting fullerene radicals do not propagate but instead can terminate. Recently, Camp *et al.* have reported the copolymerization of [60]fullerene and styrene in the presence of a large excess of the initiator AIBN.[4] According to the authors, the radicals from the initiator undergo multiple additions on [60]fullerene, ultimately changing its nature sufficiently such that it would not inhibit polymerization.

We report here findings of our study on AIBN-initiated radical polymerization of a range of vinyl monomers in the presence of [60]fullerene. The objective of this study was to determine how general is the inhibition of radical polymerization by [60]fullerene 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 studied were styrene, methyl acrylate, methyl methacrylate (MMA), acrylonitrile, vinyl acetate, 1-vinyl-2-pyrrolidone, 2-cyanoethyl acrylate (CEA) and 1-cyanovinyl acetate (CVA).

In a typical experiment, 60–100 equiv. of vinyl monomer was added to a suspension of [60]fullerene (50 mg, 0.07 mmol) in dry THF (2 ml) under argon atmosphere, followed by the addition of a catalytic amount of AIBN. The reaction mixture was heated under reflux (65 °C) for 22 h, the solvent was evaporated and the weight of the residue was taken as the first indication for the formation of a polymer. Control experiments with these monomers without [60]fullerene were also conducted under otherwise identical conditions. The results for the eight vinyl monomers studied are given in Table 1.

In the absence of [60]fullerene, polymer formation was observed in greater than 75% yield in all cases . However, in the presence of [60]fullerene, polymerization in six out of the eight monomers was substantially inhibited and yielded 15% or less of the polymeric products. For example, the reaction of methyl acrylate produced only 9% of the polymer. The presence of an α-methyl group on the vinyl moiety increases the polymer yield only marginally to 14%. Substitution with cyano, as in acrylonitrile, also did not lead to the production of substantial yields of the polymer in the presence of [60]fullerene. Surprisingly, we found that cyanovinyl acetate gave the polymer in about 50% yield. We wondered if the acetoxy group itself is responsible for this activity, but the polymerization of vinyl acetate was almost completely inhibited by [60]fullerene. Also noteworthy is the reactivity exhibited by 2-cyanoethyl acrylate (65% polymer yield), which is structurally very similar to methyl acrylate. The cyano group in this molecule is remote from the vinyl portion, and points to some cyclic intermediate in which the cyano group stabilizes the intermediate radical. It would be interesting to correlate the polymer formation with the partial reactivity factors of the various vinyl monomers. Unfortunately, we were unable to find literature reports on the partial reactivity factors for CEA and CVA, the two cases where we observed substantial copolymerization.

[60]Fullerene can inhibit the chain propagation by reacting with the initiator radical and/or by terminating the propagating chain. It has been reported that [60]fullerenes react effectively with isobutyronitrile radicals produced by the thermal decomposition of AIBN.[4] Therefore it is possible that [60]fullerene intercepts the initiating radicals in the polymerization reaction. To further understand the role of [60]fullerene as an inhibitor of propagating chains, we conducted the AIBN-initiated polymerization of MMA and quenched it with [60]fullerene at different time intervals. Polymerization of MMA was conducted for 1 or 2 h by heating 615 mg (6.14 mmol) of MMA in dry THF (2 ml) under reflux (65 °C) in the presence of 6 mg (0.036 mmol) of AIBN. Then 50 mg (0.07 mmol) of [60]fullerene was added to these reaction mixtures and heated overnight. The reaction mixture was evaporated to dryness, dissolved in MeCN, filtered to remove unconverted [60]fullerene and dried to recover the copolymers. In contrast to the complete inhibition of MMA polymerization when [60]fullerene was added at the start of the reaction, the yield of the copolymer increased to 264 mg (40%) when [60]fullerene was added following 1 h reaction, and 370 mg (56%) if the addition of [60]fullerene was delayed for 2 h. The number average molecular weights for [60]fullerene–PMMA polymers obtained in these cases were around 8,000 and 22,000 respectively. ^{13}C NMR spectra of the product do not show a peak at δ 143 corresponding to the starting [60]fullerene, which suggests complete reaction of fullerene with propagating radical chain. The low yields of polymerization in the above reactions and the difference in molecular weights further confirms that [60]fullerene quenches the propagating chains very effectively.

As mentioned above, the more reactive monomers, CVA and CEA, underwent facile copolymerization with [60]fullerene yielding 53 and 65% of the copolymers, respectively (Table 1).

Table 1 Effect of [60]fullerene on the yield of polymers from AIBN-initiated polymerization of various vinyl monomers at 65 °C

	Polymer yield (%)	
Monomer	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-vinylpyrrolidone	8	100

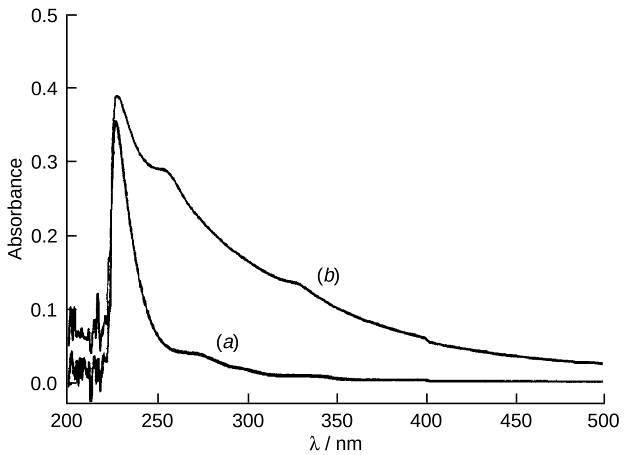

Fig. 1 UV–VIS absorption spectra of (*a*) poly(2-cyanoethylacrylate) and (*b*) the copolymer formed with [60]fullerene

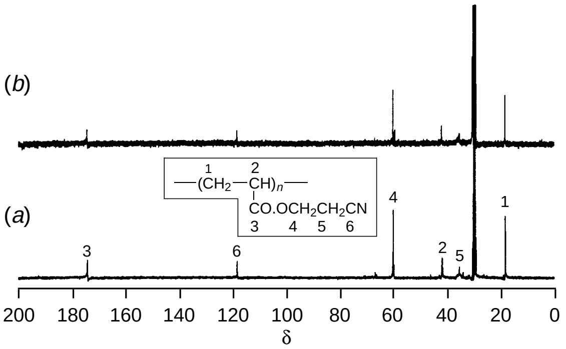

Fig. 2 ^{13}C NMR spectra of (*a*) poly(2-cyanoethyl acrylate) and (*b*) the copolymer formed with [60]fullerene

It was also observed that the initially free flowing reaction mixture became viscous as the reaction proceeded. Evidently, these monomers are reactive enough that fullerene-based radical(s) formed by the addition of a growing polymer chain can add to them and continue the polymerization process. However, before we can make this conclusion, we have to eliminate the possibility of these monomers are undergoing polymerization by a different mechanism, *e.g.* polymerization promoted by traces of moisture. Thus, we attempted polymerization of CVA and CEA in the absence of AIBN and in the presence of traces of water. In none of these cases did we observe any polymerization. Therefore we conclude that the polymerization was indeed following a radical chain pathway.

The copolymer of [60]fullerene and CVA was completely soluble in MeCN. A small amount of material that did not dissolve in MeCN was identified as [60]fullerene. In contrast, only about half of the copolymer of [60]fullerene and CEA was soluble in MeCN. We believe that the insoluble portion has either a branched or a cross-linked structure which is obtained by the multiple addition of propagating chains to the fullerene surface. We also studied the effect of [60]fullerene on the propagating chains of CEA and CVA monomers. Two experiments were conducted for each of these monomers. Polymerization was initiated by heating the monomer in dry THF in the presence of a catalytic amount of AIBN, and [60]fullerene was added to the reaction mixture after 1 h. In one experiment the reaction was quenched immediately, and in the second, the heating was continued for another 22 h. For CVA, the yield of the polymer was only 18% when the reaction was quenched immediately after adding [60]fullerene, and 50% when the mixture was heated for the additional 22 h. These results further show that [60]fullerene does not completely inhibit the polymerization of reactive monomers. CEA, being an even more reactive substrate, yielded 83% of the polymer in the first hour and continued heating after the addition of [60]fullerene did not increase the yield any further. Analogous reactions with MMA yielded 24% of polymer after the first hour and 40% of the polymer if the mixture was heated overnight compared to 98% of the polymer after 22 h in the absence of [60]fullerene and 14% of polymer in the presence of [60]fullerene.

Structural characterization of the copolymers was performed using IR, NMR and UV spectroscopic techniques and thermogravimetric analysis (TGA). The presence of fullerene moieties is evident from the absorption spectra of the copolymers of [60]fullerene with CEA and CVA. Fig. 1 shows the absorption spectra for poly(CEA) and the copolymer formed with [60]fullerene. Whereas the absorption bands of the homopolymers cut off at much shorter wavelengths, the copolymers show broad overlapping bands extending from the UV region to almost 500 nm. Sun and coworkers[2] have also observed a similar broadening of the characteristic absorption bands of fullerenes when incorporated into a polymer matrix. Analogous data (not shown) were obtained for the CVA system. Fig. 2 shows the identical ^{13}C NMR spectra of the homopolymer and the copolymers for CEA. The spectrum for the copolymer does not show any signals due to the [60]fullerene moiety. The absence of any fullerene peaks may be due to the fact that the concentration of the fullerene units is very low, which is further exacerbated by the loss of the 60-fold degeneracy of the original [60]fullerene once it has undergone reaction to produce adducts. However, it is also significant that there is no peak at δ 143, corresponding to *free* [60]fullerene, in the case of the copolymer. Thus, the extended UV absorption must be due to the fullerene units that are now a part of the polymer. Again, similar data (not shown) were obtained for the CVA system. 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 the fullerene copolymers when compared to the homopolymer.

We therefore conclude that [60]fullerene acts as an efficient inhibitor or a retarder in the radical polymerization of most vinyl monomers and results in the formation of [60]fullerene-terminated structures. However, with certain reactive vinyl monomers such as cyanoethyl acrylate and cyanovinyl acetate, it can form copolymers. Evidently, these monomers can add to the fullerene-based radical intermediate to propagate the polymerization. The role of reactivity ratios and general dependence on the structural and chemical nature of the vinyl monomers on polymerization reaction in the presence of [60]fullerene is currently under investigation in more detail in our laboratory.

This work was conducted under the program, ‘Advanced Chemical Processing Technology’, consigned to the Advanced Processing Technology Research Association from the New Energy and Industrial Technology Development Organization, which is carried out under the Industrial Science and Technology Frontier Program administered by the Agency of Industrial Science and Technology, the Ministry of International Trade and Industry, Japan.

References

1 T. Cao and S. Webber, *Macromolecules*, 1995, **28**, 3741.
2 C. E. Bunker, G. E. Lawson and Y.-P. Sun, *Macromolecules*, 1995, **28**, 3744.
3 R. D. McClain, *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. R. S. Ruoff and K. M. Kadish, Electrochemical Society, Pennington, NJ, 1995, p. 71.
4 A. G. Camp, A. Lary and W. T. Ford, *Macromolecules*, 1995, **28**, 7959.

Received, 8th August 1996; Com. 6/05555I