Lattice-type Polymers from an Adduct of [60]Fullerene and 2-Methylaziridine

A. Nigam,[a] T. Shekharam,[a] T. Bharadwaj,[a] J. Giovanola,[b] S. Narang[a] and R. Malhotra*[c]

[a] *Chemistry Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California, 94025, USA*
[b] *Poulter Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California, 94025, USA*
[c] *Molecular Physics Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California, 94025, USA*

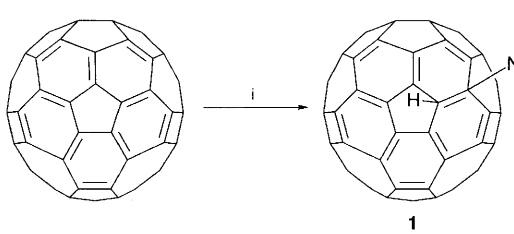
An adduct of [60]fullerene and 2-methylaziridine (approx. composition 1:10) is prepared and copolymerized with Novolac, Epon and Bisphenol A to obtain three dimensional polymers containing [60]fullerene with low coefficients of friction and good wear properties, which bode well for their potential use as solid lubricants.

The isolation[1] of [60]fullerene as a stable allotrope of carbon and its subsequent production[2] in macroscopic amounts prompted numerous studies, as can be judged by the number of recent publications in this area. Its soccer ball-like structure and high electron affinity prompted several research groups[3] to develop new chemistry for its functionalization. Along with the development of its chemistry, several different polymers incorporating [60]fullerene have been reported.[4] Amato[5] proposed that polymers of [60]fullerene could be of two different structural kinds: (i) 'pearl necklace', in which the [60]fullerene 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[3b] proposed a lattice-type polymer, which is a two- or three-dimensional variant of the 'pearl necklace' polymers. Herein we report a simple synthesis of an adduct of 2-methylaziridine and [60]fullerene, and the preparation of lattice-type polymers from it *via* ring-opening polymerization.

Prompted by the work of Wudl[3d] and coworkers showing the facile addition of amines to [60]fullerene, we investigated the addition of 2-methylaziridine to [60]fullerene. Our motivation behind this study was the recognition that aziridine moieties would allow incorporation of the [60]fullerene cage into a variety of polymers.[6] This approach is particularly interesting from a processing point of view because it does not lead to any by-products during polymerization, and hence could be directly used to produce films and coatings with novel mechanical, optical and electromechanical properties.

The adduct was synthesized by stirring [60]fullerene in dry benzene with an excess of freshly distilled 2-methylaziridine for several days.† Initially the reaction mixture was purple and had excess [60]fullerene particles suspended in it (Scheme 1). As the reaction progressed the mixture became dark brown and finally turned into a very clear reddish–brown homogeneous solution. Upon evaporation of the solvent the adduct **1** was left as a shining dark-brown solid. (For the sake of clarity only one methylaziridine ring is shown in Scheme 1, although the adduct on average has ten such rings.)

Unlike the starting [60]fullerene, the adduct was readily soluble in chloroform, tetrahydrofuran, benzene and toluene. The mass gain observed in the reaction (72.5%) suggests the adduct to have an average composition of about 1:10 [60]fullerene–methylaziridine, *viz.*, $C_{60}{\cdot}(C_3H_7N)_{10}$. The elemental analysis is also consistent with the addition of ten aziridine rings.‡ The calculated values (C, 83.69; H, 5.46; N, 10.84%) are in close agreement with those found (C, 82.96; H, 5.48; N, 11.56%). Although we expected a mixture of products with varying numbers of methylaziridine rings added to [60]fullerene, the HPLC of the crude reaction product on a dinitroanilinopropyl phase with 1:1 toluene–hexane exhibited a single main peak.[7] Thus, we surmise that a single component, possibly the 10:1 adduct, was dominant in the reaction product. The FTIR spectrum of the adduct was dominated by peaks due to the aziridine rings, such as those at 1443 and 1396 cm^{-1} due to CH_2 deformations, at 1238 cm^{-1} due to asymmetric ring deformations, and at 1054 cm^{-1} due to C–N stretching deformations. Although the proton NMR showed only broad peaks at the expected chemical shifts, the ^{13}C NMR showed sharp lines due both to the aziridine rings and to the [60]fullerene nucleus. Mass spectrometric analysis of the adduct by FAB-MS and by surface analysis by laser ionization (SALI) gave peaks at 777, 834, 891 and 948 Da (1 Da ≈ 1.66×10^{-27} kg) corresponding to the addition of one to four aziridine units to [60]fullerene. As with many other addition products of fullerene, mass spectral analysis is accompanied by substantial fragmentation, and peaks due to [60]fullerene with five and more aziridine units were not seen. In addition to the peaks mentioned, there was a prominent peak at 720 Da corresponding to [60]fullerene. Because there was no unconverted [60]fullerene in the reaction product, the peak at 720 Da is due to a fragment of the adduct and its presence indicates that the overall cage structure of [60]fullerene has been preserved.



1

Suspension in purple solution   Clear brown solution

Scheme 1 *Reagents and conditions*: i, 2-methylaziridine (30 equiv.), benzene, room temp., several days

The aziridine rings are very susceptible towards nucleophilic addition, and we expected it to be possible to crosslink phenolic compounds like Novolac or Bisphenol A and epoxides like Epon 828 with **1**. Accordingly, we prepared several polymers with these materials by heat curing them with varying amounts of the adduct (Table 1).§ The thermal stability of the resulting polymers was assessed by TGA. As can be seen from Table 1 a prepolymer like Novolac loses 57% of its weight when heated to 400 °C in an Ar atmosphere. When the same Novolac is cured with the adduct **1** in the ratio 2:1, it loses only 26% of its mass under the same conditions.

Though the mass loss in the case of Epon 828 and Bisphenol A cannot be compared with the polymers since they are only

Table 1 Thermal and mechanical properties of polymers with [60]fullerene–2-methylaziridine adduct

Polymer sample		Curing conditions		Mass loss at 400 °C	
Resin	Resin:Adduct	T/°C	t/h	(%)	Coefficient of friction[a]
Novolac		180	18	57	0.20 → 0.35
Novolac	(10:1)	180	18	30	0.15 → 0.40
Novolac	(6:1)	180	18	28	0.20 → 0.45
Novolac	(2:1)	180	18	26	0.15
Epon 828		—	—	95	—
Epon 828	(10:1)	200	18	65	0.35 → 0.60
Epon 828	(6:1)	200	18	42	0.15 → 0.50
Epon 828	(2:1)	200	18	18	0.15–0.20
Bisphenol A		—	—	98	—
Bisphenol A	(1:1)	200	18	3	0.30 → 0.55

[a] $X \rightarrow Y$ means the initial friction coefficient value X deteriorates to value Y.

monomers, the TGA data clearly shows the thermal stability of these polymers. The effect of the amount of the adduct on the *thermal* stability of the polymer is illustrated by the Epon polymers. Whereas a 10:1 ratio of epon–adduct gives a polymer which loses 65% of its weight by heating to 400 °C, 6:1 and 2:1 polymers lose only 42 and 18%, respectively of their mass under similar conditions.

To study the friction and wear behaviour of the polymers, thin films were made by spin coating a very concentrated DMF–toluene solution of the reactants onto small quartz discs and heat curing them in a hot air oven. All the films were brown, transparent and on a pencil scale were very hard (generally >9H). The friction and wear behaviour studies were made using a pin on disc arrangement using a tilted, bevelled, flat-bottomed silicon nitride pin sliding on the coated quartz disc.[8]

Novolac and Epon 828 resins containing high concentration of the adduct (2:1) gave films of low friction coefficients (0.15–0.20), comparable to that of wet graphite. We have also observed indications that a coating in the process of breaking down during the sliding friction test regenerated itself. This ability to regenerate the interface film is a characteristic feature of good solid lubricants such as graphite or molybdenum disulfide. Films made with lower concentrations of the adduct initially gave friction coefficients of 0.15–0.20, but rapidly degraded to 0.50 in a matter of seconds. Films made of Bisphenol A also wore off rapidly, even with high concentrations of the [60]fullerene–methylaziridine adduct.

In conclusion, we have shown that 2-methylaziridine undergoes facile multiple additions with [60]fullerene to give an adduct that reacts readily with phenolic and epoxy monomers *via* aziridine ring opening to produce polymers with good thermal stability. By simple spin coating the polymers produce hard transparent lubricant films which exhibit friction behaviour similar to that of wet graphite powder. Currently we are exploring the utility of **1** for the synthesis of several other classes of polymers from fluorinated monomers and siloxanes containing hydroxy, amino, and thiol functional groups.

This work was conducted under the program 'Advanced Chemical Processing Technology', consigned to ACTA from New Energy and Industrial Development Organization (NEDO), which is carried out under the Industrial Science and Technology Frontier Program enforced by the Agency of Industrial Science and Technology, the Ministry of International Trade and Industry (MITI), Japan.

Received, 24th April 1995; Com. 5/02576A

Footnotes

† Synthesis of [60]fullerene–2-methylaziridine adduct: To a suspension of 400 mg of [60]fullerene in 20 ml of dry benzene was added 1 ml (excess) of 2-methylaziridine under Ar and stirred at room temp. for 4 d. The initially violet heterogeneous reaction mixture became dark brown as the reaction proceeded and turned to a very clear deep reddish-brown solution by the end of the reaction. Upon removal of solvent and excess aziridine under reduced pressure 691 mg of the adduct **1** was obtained as a shining dark-brown solid (mp 204 °C, from DSC).

‡ Satisfactory elemental analysis was obtained. FTIR (KBr disc) ν/cm^{-1}: 1443, 1396, 1364 (CH_2), 1238 (asymmetric ring deform.), 1054 (C–N). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: Two broad peaks at 1.2 and 2.0 for 5 and 2 H, respectively. ^{13}C NMR {[$^{2}H_6$]benzene containing 0.035 mol dm^{-3} $Cr(acac)_3$, 75 MHz} δ: 18.3 br (N–*C*H_2), 21.6 (*C*–CH_3), 34.0 (C_{60}*C*H), 34.5 (*C*H_3), 34.4 (C_{60}*C*–N), 142–152 (several peaks due to C_{60} nucleus). UV ($CHCl_3$) λ/nm: 300 sh, 410 (shoulder) SALI (surface analysis by laser ionization): 777 [$C_{60}(C_3H_7N)_1$], 834 [$C_{60}(C_3H_7N)_2$], 891 [$C_{60}(C_3H_7N)_3$], 948 [$C_{60}(C_3H_7N)_4$].

§ Representative procedure for preparation of polymers from the [60]fullerene–2-methylaziridine adduct: Novolac (100 mg) was dissolved in 0.5 ml of *N,N*-dimethylformamide in a small sample vial. In another sample vial [60]fullerene–methylaziridine adduct (10 mg) was taken and dissolved in 0.25 ml toluene. This solution was added to the Novolac solution and mixed thoroughly. The resulting solution is then spin coated onto a one inch diameter quartz disc and heated in a hot air oven at 180 °C overnight to produce a brown film on the quartz disc.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.

2 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.

3 For reviews on chemistry of fullerene, see: (*a*) G. A. Olah, I. Busci, R. Aniszfeld and G. K. Suryaprakash, *Carbon*, 1992, **30**, 1203; (*b*) R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; (*c*) F. Diedrich, L. Isaacs and D. Philp, *Chem. Soc. Rev.*, 1994, 243; (*d*) *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*, ed. G. Hammond and V. J. Kuck, *ACS Symp. Ser.* 481, American Chemical Society, Washington DC, 1992.

4 For polymers incorporation [60]fullerene, see: E. T. Samulski, J. M. Desimone, M. O. Hunt, Y. Z. Menceloglu, R. C. Jarnagin, G. A. York, K. B. Labat and H. Wang, *Chem. Mater.*, 1992, **4**, 1153; A. O. Patil, G. W. Schriver, B. Cartensen and R. D. Lundberg, *Polym. Bull.*, 1993, **30**, 187; D. E. Bergbreiter and H. N. Gray, *J. Chem. Soc., Chem. Commun.*, 1993, 645; S. Shi, K. C. Khemani, C. Li and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 10656; K. L. Wooley, C. J. Hawker, J. M. J. Frechet, F. Wudl, G. Sradanov, S. Shi, C. Li and M. Kao, *J. Am. Chem. Soc.*, 1993, **115**, 9836.

5 I. Amato, *Science*, 1991, **254**, 30.

6 S. C. Narang, S. C. Ventura, S. Ganapathiappan, T. R. Bhardwaj and A. Nigam, *US Pat.* 5 367 051, 1994, assigned to SRI International.

7 D. S. Tse, R. S. Ruoff, D. C. Lorents and R. Malhotra, *Preparative and Semipreparative HPLC of Fullerenes on Silica-bonded Dinitroanilinopropyl Phase*, in *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. K. M. Kadish and R. S. Ruoff, The Electrochemical Society, Pennington, New Jersey, 1994, p. 191.

8 E. Rabinowicz, *Friction and Wear of Materials*, Wiley, New York, 1965.