

Comparative Raman study of photopolymerized and pressure-polymerized C₆₀ films

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We have made a Raman study of low-pressure polymerized and photopolymerized C₆₀ films, polymerized in different ways, but otherwise initially identical. Although the structures developing in the films during polymerization are initially very similar, an analysis of characteristic features in the Raman spectra shows that photopolymerized material forms a more complex polymeric structure when the polymerization approaches saturation. We suggest that this complex structure contains branched polymeric chains and in particular that a mode near 1454 cm⁻¹ in photopolymerized C₆₀ is characteristic for this type of structure.

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In the last few years the polymeric phases of C₆₀ have been shown a lot of interest. There are basically three routes that can be used to polymerize C₆₀. If thin films are irradiated with visible or ultraviolet light, the material is phototransformed,¹ in which case some of the double bonds on the molecules break up and by a 2 + 2-cycloaddition form bonds to neighboring molecules.¹ In this process it has been reported that the lattice constant shows a contraction from 14.17 Å in pristine C₆₀ to 13.80 Å.² Another way to polymerize C₆₀ is by treating the material at high pressure and elevated temperatures, which gives a bulk polymerized material.³ A number of different studies show that depending on the temperature and pressure, both one- and two-dimensional polymeric structures can be obtained.²⁻⁷ Finally a third way to polymerize C₆₀ is by doping the material with alkali metals, which usually results in a one-dimensional polymeric structure.⁸ The structures of the pressure polymerized and the alkali-metal-doped C₆₀ are relatively well known through earlier studies.²⁻⁸ However, since the photopolymerization can only be carried out on thin films the detailed structure of that phase is not yet known. In recent years we have studied the low-pressure polymerized phase that is obtained near 1 GPa and 570 K. This phase is often very disordered, but has been shown to consist of mainly one-dimensional clusters (chains) which leads to an orthorhombic distortion of the original fcc structure.^{3-5,9,10}

In this study we have analyzed polymerized C₆₀ films with Raman spectroscopy, a very powerful tool to study the polymerization of C₆₀. When the material is polymerized, many of the original ten Raman active modes split and shift and new modes appear due to the lowering of the symmetry.¹¹ We have shown earlier that when thin films are partially polymerized by irradiation with light or by treatment at high pressure and elevated temperatures they form structures that are initially very similar judged from the Raman spectra of the two films.¹² In this work we present a similar but more detailed study in which we have compared

the Raman spectra for thin films polymerized with the same two methods when the polymerization in the two films has been driven as far as possible toward saturation.

The thin films were made in identical pairs by evaporating pristine C₆₀ with a purity of 99.98%, obtained from Term USA, Berkeley, CA, at about 500 °C on adjacent quartz or mica substrates. To improve the film quality the substrates were kept at 150 °C. The thickness of the films were recorded by a standard piezocrystal gauge. The films had a diameter of 1.0 cm and a thickness of between 0.5 and 1.0 μm. After the evaporation step the films were placed in glass tubes, which were evacuated and sealed off with a torch. The photopolymerization was carried out with an Ar⁺ ion-laser (514 nm) with a power of 150 mW/cm² for up to five days. The polymerization state was monitored by Raman spectroscopy as described below and the treatment was continued until no further evolution with time could be observed. The low laser power was used to ensure that the film temperature was kept close to room temperature.

For the pressure polymerization we have used a piston-cylinder device with a Teflon pressure cell containing an internal heater. The films were placed in the pressure cell under an argon atmosphere in a glove box to avoid exposure to air. To ensure hydrostatic conditions we have used a low-viscosity silicon oil as pressure medium. The pressure polymerization was carried out at 1.0 GPa and 570 K for five hours, a time long enough to saturate the polymerization in other pressure treated bulk C₆₀ samples.⁹ At this pressure and temperature an orthorhombic structure is expected^{4,5} but in practice the structure is often very disordered.²

The pristine and polymerized C₆₀ films were analyzed with Raman spectroscopy using a Bruker Fourier transform (FT)-Raman with a Nd-YAG laser (1064 nm) with a power of 50 mW. With this laser we have the advantage that we do not induce any further photopolymerisation of the films.

The Raman spectrum of pristine C₆₀ contains 10 different mode frequencies, 8 fivefold degenerate H_g modes and 2

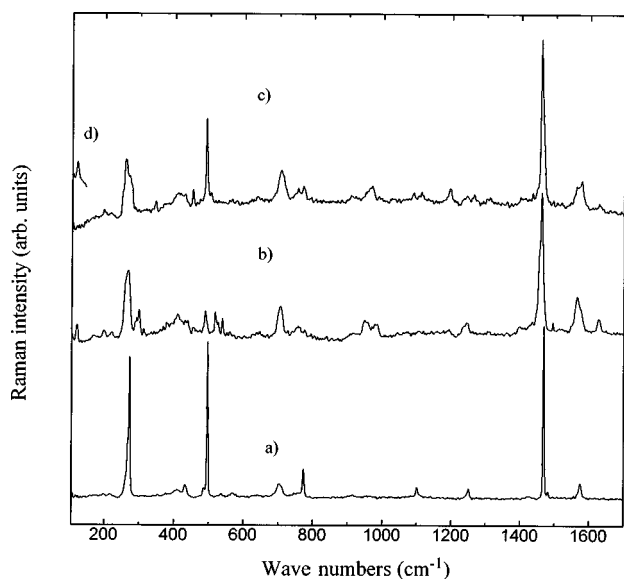


FIG. 1. Raman spectra between 100 and 1700 cm^{-1} for (a) pristine C_{60} , (b) photopolymerized C_{60} film on mica substrate, and (c) pressure polymerized C_{60} film on mica substrate. Curve (d) shows a small region around the mode at 120 cm^{-1} for a pressure polymerized C_{60} film on a quartz substrate.

single degenerate A_g modes. When C_{60} is polymerized the H_g modes split due to the lowering of the symmetry and the A_g modes shift in frequency. In addition to this, new modes that were previously optically silent appear in the spectrum.

It has been shown earlier that when the material is polymerized to about 50% the Raman spectra for the pressure and photopolymerized materials are almost identical, regarding both mode intensities and positions.¹² This indicates that the initial polymeric structures are very similar in the films polymerized with the two completely different methods.

Figure 1 shows the Raman spectra for pristine, photopolymerized and pressure polymerized C_{60} films between 100 and 1700 cm^{-1} . The polymerization is saturated in the latter two samples (see below). Many new modes appear in the Raman spectra of both the photopolymerized and pressure polymerized films. Several peaks have also broadened significantly. New modes can be seen for example around 950 cm^{-1} , a frequency range corresponding to the vibrations in the four-membered intermolecular rings formed in the $2+2$ cycloaddition,¹³ and also for the photopolymerised film in the low frequency region at 120 cm^{-1} . The latter mode is assigned to the intermolecular mode between the C_{60} molecules in the polymeric chain.¹ The 120 cm^{-1} mode is very weak in the spectrum observed for the pressure polymerized film on a mica substrate but can be seen clearly in curve (d), which shows a small region of the Raman spectrum for a pressure polymerized film on a quartz substrate. It is not clear why this mode does not show up in the sample on the mica substrate but it is known from earlier experiments that pressure polymerized films and powder samples often have very weak intermolecular modes in the Raman spectrum.¹² Although the low apparent intensities of these modes might be due to a high background in the films, covering the low-frequency modes, the fact that strong low-frequency modes

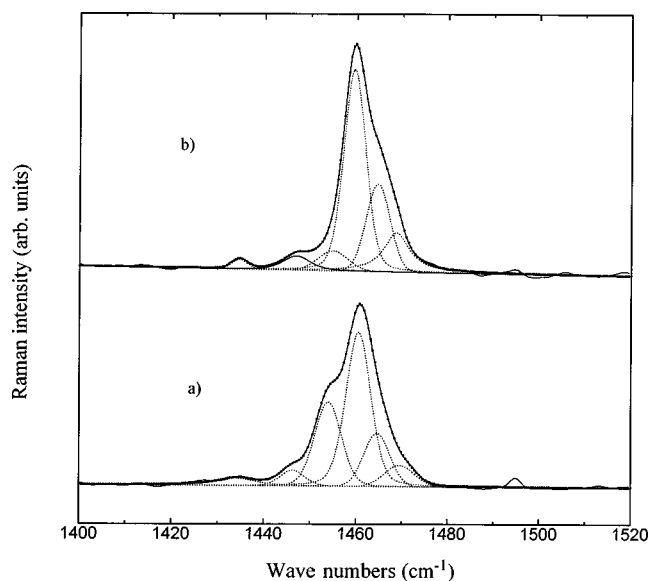


FIG. 2. Raman spectra between 1400 and 1520 cm^{-1} , showing the pentagonal pinch mode for, (a) photopolymerized C_{60} film on mica substrate and (b) pressure polymerized C_{60} film on mica substrate. Dotted curves indicate individual fitted components.

are observed in polymerized single crystals¹⁴ indicates that the difference may be due to a less well developed long-range order in the films.

The pentagonal pinch $A_g(2)$ mode at 1469 cm^{-1} has proven to be a particularly reliable probe of the polymerization state,^{3,9,15} because the shift of this mode is very sensitive to the number of covalent bonds on the C_{60} molecules. For dimers the $A_g(2)$ mode shifts to 1464 cm^{-1} ,¹⁶⁻¹⁸ for longer chains it shifts to 1460 cm^{-1} (Refs. 15 and 17) and for two-dimensional structures it shifts even further.^{2,19,20}

To resolve the peaks in the region of the pentagonal pinch mode we have used a peak-fitting program and fitted Voigt line shapes. Looking at the positions and intensities of the different components in Fig. 2 we see a clear difference between the photopolymerized and the pressure-polymerized films. Despite the very long polymerization time both films show a small component at 1469 cm^{-1} , representing a small fraction of unpolymerized material. The other peaks are positioned at 1464 , 1460 , 1454 , 1447 , and 1434 cm^{-1} for both films. However, looking at the relative intensities of the components, tabulated in Table I, there are some significant differences, the most obvious of which occurs for the component at 1454 cm^{-1} , which is much larger (24.6%) for the photopolymerized film than for the pressure polymerized one (6.12%). No such feature was observed for partially polymerised films.¹² Comparing the mode intensities at 1464 and 1460 cm^{-1} , which are assigned to dimers and longer polymeric chains, respectively, it is seen that the samples contain roughly equal amounts of polymeric chains but that the pressure polymerized film contains more dimers than the photopolymerized film. This differs from the results in a previous report by Lopinski, Fox, and Lannin²¹ who suggested that photopolymerized C_{60} mainly consisted of dimers and to a small extent trimers. It should be noted, however, that the ratio of dimers to longer chains depends strongly on both polymerization time⁹ and temperature.¹⁷

Small components at 1447 and 1434 cm^{-1} are present in

TABLE I. Intensity and position for the individual components of the pentagonal pinch mode, fitted with Voigt line shapes, for the pressure and the photopolymerized film. The numbers in parentheses show the full width at half maximum (FWHM) for each component.

Photopolymerized	Percentage of total peak area	Pressure polymerized	Percentage of total peak area	Assigned to ^{ref.}
1434.2 cm ⁻¹ (10)	4.53	1434.6 cm ⁻¹ (4.0)	1.49	polymeric planes ^{a,b,c}
1446.3 cm ⁻¹ (6.1)	4.50	1447.0 cm ⁻¹ (7.0)	5.00	polymeric planes ^{a,b,c}
1454.0 cm ⁻¹ (6.8)	24.9	1454.8 cm ⁻¹ (7.6)	6.12	branched chains?
1460.5 cm ⁻¹ (6.4)	45.0	1459.6 cm ⁻¹ (5.6)	50.5	linear chains ^{d,e}
1464.6 cm ⁻¹ (6.6)	14.4	1464.7 cm ⁻¹ (6.1)	21.6	Dimers ^{e,f,g}
1469.6 cm ⁻¹ (7.7)	6.7	1468.8 cm ⁻¹ (6.6)	15.4	Pristine C ₆₀

^aReference 2.

^bReference 19.

^cReference 20.

^dReference 15.

^eReference 17.

^fReference 16.

^gReference 18.

equal amounts in both samples. The former of these has been assigned to a two-dimensional polymeric structure obtained at higher pressure and higher temperatures.^{2,19,20} The latter has also been observed in two-dimensional (2D) polymers² but might be a shifted and broadened $H_g(7)$ mode, located at 1426 cm⁻¹ in pristine C₆₀. The very low intensities imply that none of the samples has formed a predominantly two-dimensional polymeric structure, as has been proposed for C₆₀, photopolymerized for very long time.²² All modes in the vicinity of the pentagonal pinch mode can therefore be assigned to well-defined polymeric structures (dimers, chains and planes) except the mode at 1454 cm⁻¹, which seems to be characteristic for the photopolymerized material only. This was previously also noted by Rao *et al.*² Since this mode is also absent in the Raman spectra for two-dimensionally polymeric structures^{2,19,20} it is unlikely that it represents polymeric planes.

It is reasonable to believe that the internal mechanical stress in photopolymerized material is larger than in pressure polymerized material since no external force is applied to guide the direction of the necessary volume contraction during polymerization and the reaction thus proceeds in random directions. One possibility could therefore be that the mode located at 1454 cm⁻¹ could be assigned to branched polymeric chains. The shift of the pentagonal pinch mode as a function of cluster size and cluster form has been calculated by Porezag *et al.*²³ who show that the $A_g(2)$ mode shifts in proportion to the number of intermolecular covalent bonds formed on the molecule. Since we know experimentally that the formation of dimers (two bonds per molecule) results in a shift of about 5 cm⁻¹, the formation of linear chains (four bonds per molecule) results in a shift of 10 cm⁻¹, and the formation of the tetragonal phase (8 bonds per molecule) in a shift of 21 cm⁻¹, it is reasonable to suggest that a shift of 15 cm⁻¹ represents a structure containing six covalent bonds per molecule. This would correspond to a structure containing branched one-dimensional chains or linear chains with a high density of molecules grafted on to random sites along its sides.

A structure containing more branched chains has a lower symmetry than a structure containing better-ordered straight

polymer chains. This should lead to an increased splitting of the H_g modes, and such a difference is indeed observed in Fig. 3, which shows the region around the $H_g(1)$ mode for the two types of polymerized films. Both spectra in the figure show a very clear splitting of the fivefold degenerate $H_g(1)$ mode indicating a lower symmetry for both samples than for pristine C₆₀. However, in the Raman spectrum for the photopolymerized film the $H_g(1)$ mode is clearly much more spread out with new components present even up to 299 cm⁻¹, indicating an even lower symmetry in this sample than in the pressure polymerized one.

In conclusions, we have analyzed characteristic features in the Raman spectra for pressure and photopolymerized C₆₀ films and found that both types of materials contain mainly long polymeric chains and dimers when polymerized until saturation. The Raman spectrum for the photopolymerized film differs from that of the pressure polymerized film in

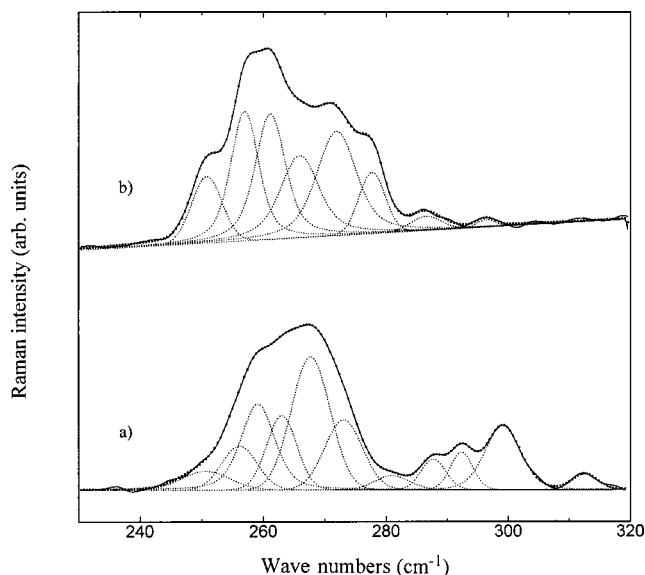


FIG. 3. Raman spectra between 230 and 320 cm⁻¹, showing the split $H_g(1)$ mode for (a) photopolymerized C₆₀ film on mica substrate and (b) pressure polymerized C₆₀ film on mica substrate. Dotted curves indicate individual fitted components.

containing a characteristic mode at 1454 cm^{-1} , which cannot be assigned to either dimers, linear polymer chains, or two-dimensionally polymerized structures. We tentatively assign this mode to branched polymeric chains in general agreement with calculations by Porezag *et al.*²³ The presence of such chain defects implies a larger disorder and thus a lower symmetry in the photopolymerized phase. This should lead to a more pronounced split of the $H_g(1)$ mode and the ap-

pearance of new modes in the region around the original $A_g(1)$ mode, and such features are also observed in the samples studied here.

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- ¹A. M. Rao, P. Zhou, K. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, *Science* **259**, 955 (1993).
- ²A. M. Rao, P. C. Eklund, J.-L. Hodeau, L. Marques, and M. Nunez-Regueiro, *Phys. Rev. B* **55**, 4766 (1997).
- ³Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, Jr., A. F. Hebard, R. Tyccko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, *Science* **264**, 1570 (1994).
- ⁴R. Moret, P. Launois, P.-A. Persson, and B. Sundqvist, *Europhys. Lett.* **40**, 55 (1997).
- ⁵V. Agafonov, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, A. Kahn-Harari, P. Dubois, R. Céolin, and H. Szwarc, *Chem. Phys. Lett.* **267**, 193 (1997).
- ⁶M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Bethoux, and M. Perroux, *Phys. Rev. Lett.* **74**, 278 (1995).
- ⁷L. Marques, J.-L. Hodeau, M. Núñez-Regueiro, and M. Perroux, *Phys. Rev. B* **54**, 12 633 (1996).
- ⁸S. Pekker, A. Janossy, L. Mihaly, O. Chauvet, M. Carrard, and L. Forro, *Science* **265**, 1077 (1994).
- ⁹P.-A. Persson, U. Edlund, P. Jacobsson, D. Johnels, A. Soldatov, and B. Sundqvist, *Chem. Phys. Lett.* **258**, 540 (1996).
- ¹⁰B. Sundqvist, O. Andersson, U. Edlund, Å. Franson, A. Inaba, P. Jacobsson, D. Johnels, C. Meingast, R. Moret, T. Moritz, P.-A. Persson, A. Soldatov, and T. Wågberg, in *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes*, edited by K. M. Kadish and R. S. Ruoff (Electrochemical Society, Pennington, NJ, 1997), Vol. 3, p. 1024.
- ¹¹M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996), Chap. 11.
- ¹²T. Wågberg, P.-A. Persson, P. Jacobsson, and B. Sundqvist, *Appl. Phys. A: Mater. Sci. Process.* **64**, 223 (1997).
- ¹³F. A. Miller, R. J. Capwell, R. C. Lord, and D. G. Rea, *Spectrochim. Acta* **A28**, 603 (1972).
- ¹⁴P.-A. Persson, O. Andersson, P. Jacobsson, A. Soldatov, B. Sundqvist, and T. Wågberg, *J. Phys. Chem. Solids* **58**, 1881 (1997).
- ¹⁵P. C. Eklund, P. Zhou, K.-A. Wang, G. Dresselhaus, and M. S. Dresselhaus, *J. Phys. Chem. Solids* **53**, 1391 (1992).
- ¹⁶S. Lebedkin, A. Gromov, S. Giesa, R. Gleiter, B. Renker, H. Rietschel, and W. Krätschmer, *Chem. Phys. Lett.* **285**, 210 (1998).
- ¹⁷B. Burger, J. Winter, and H. Kuzmany, *Z. Phys. B* **101**, 227 (1996).
- ¹⁸T. Wågberg, P.-A. Persson, B. Sundqvist, and P. Jacobsson, in *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes* (Ref. 10), Vol. 5, p. 674.
- ¹⁹V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. Agafonov, H. Allouchi, R. Ceolin, A. V. Dzyabchenko, V. M. Senyavin, and H. Szwarc, *Phys. Rev. B* **58**, 14 786 (1998).
- ²⁰T. Wågberg, A. Soldatov, and B. Sundqvist (unpublished).
- ²¹G. P. Lopinski, J. R. Fox, and J. S. Lannin, *Chem. Phys. Lett.* **239**, 107 (1995).
- ²²J. Onoe and K. Takeuchi, *Phys. Rev. Lett.* **79**, 2987 (1997).
- ²³D. Porezag, M. Pederson, and Th. Frauenheim and Th. Köhler, *Phys. Rev. B* **52**, 14 693 (1995).