High pressure photoinduced polymerization of the orthorhombic polymeric phase of C_{60}

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Abstract

The stability of the linear orthorhombic polymer of C_{60} as a function of pressure has been studied by Raman scattering and X-ray measurements. The in situ Raman study shows an irreversible transition to a new phase occurring at pressures as low as ~0.3 GPa. The specimens treated at pressure up to 3 GPa without laser irradiation do not show any structural changes after pressure release. The Raman spectrum of the new phase differs from those of the known 2D polymerized phases of C_{60}. These data indicate that the simultaneous application of pressure and laser irradiation results in pressure photoinduced polymerization of the pristine polymeric chains of C_{60} thus transforming it to a new polymeric phase of C_{60}.
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1. Introduction

The treatment of C_{60} under high pressure and high temperature leads to its 1D, 2D or 3D polymerization related to intermolecular covalent bonding via sp^3-like coordinated carbon atoms. The crystal structures based on the 1D, 2D and 3D polymers of C_{60} have been identified as the orthorhombic (1D-O), tetragonal (2D-T) and rhombohedral (2D-R), and face-centred cubic (3D-fcc) [1–5].

The number of sp^3-like coordinated C atoms per C_{60} cage increases from 4 to 8 and to 12 for 1D-O, 2D-T and 2D-R phases, respectively. Numerical calculations have predicted that three-dimensional polymerization might occur by application of uniaxial pressure perpendicular to the polymeric chains (sheets) of the linear (planar) polymers of C_{60} [6,7]. The planar 2D-T polymer under pressure of ~20 GPa transforms to 3D-polymer with 24 sp^3-like coordinated carbon atoms per C_{60} molecule via covalent bonding between molecules in adjacent polymeric sheets [6].

Another calculation predicted that uniaxial compression of linear and planar polymers of C_{60} leads to 3D polymerization with 52, 56, and even 60 sp^3-like coordinated carbon atoms per C_{60} molecular cage [7]. Experimental in situ Raman and X-ray studies [8,9] of the 2D-T polymer at high pressure have revealed an irreversible transition above 20 GPa to an ordered high-pressure phase, related to further three-dimensional polymerization of the 2D-T polymer via covalent bonding of molecules belonging to adjacent polymeric sheets. The in situ Raman studies of the 2D-R polymer at high pressure have revealed an irreversible transition near 15 GPa to a disordered high-pressure phase [10], also related to three-dimensional polymerization via chaotic bonding of molecules belonging to adjacent polymeric sheets.

In this Letter, we have studied the stability of 1D-O polymer of C_{60} at high pressure and at room temperature by means of in situ Raman scattering at high pressure, as well as by the X-ray analysis of the crystal structure of the 1D-O polymer before and after pressure application. It is important to note that at ambient conditions the 1D-O polymer is stable with respect to laser irradiation

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at moderate laser intensities that prevent the sample over-heating. The high-pressure experiments were undertaken to verify the predicted pressure-induced transformation of the linear polymer related to further polymerization via covalent bonding between molecules belonging to adjacent polymeric chains.

2. Experimental

Samples of the initial 1D-O phase were prepared from sublimed 99.98% pure C_{60} powder at 1.2 GPa at 573 K in a 'toroid'-type device. The preliminary X-ray analysis has confirmed that the samples have the orthorhombic packing of linear polymeric chains (space group P_{mnn}: $a = 9.098$ Å, $b = 9.831$ Å, and $c = 14.72$ Å). The specimens used for the high pressure measurements had dimensions of ∼100 μm and have been selected from the batch material by means of micro-Raman probing for their intense, clear and spatially uniform Raman spectra, typical of the 1D-O polymeric phase [11].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectra were taken in the back-scattering geometry by the use of the micro-Raman system comprising an OLYMPUS microscope equipped with objective of 20× magnification and a spatial resolution of ∼8 μm. The spectral width of the system was ∼5 cm^{-1}. The 514.5 nm line of an Ar^+ laser with beam power below 2 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out using a Mao-Bell type diamond anvil cell [12]. The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [13].

3. Results and discussion

The Raman spectrum of the initial 1D-O polymer at ambient conditions is shown in Fig. 1a. The number of the Raman active modes and the peak positions are typical for 1D-O polymeric phase and are very close to those reported earlier [11]. Fig. 1c shows the spectrum of the same specimen at initial pressure ∼0.69 GPa taken during the first series of the high-pressure Raman measurements. The spectrum has quite different structure: the number of peaks is increased and the peak positions are changed drastically with respect to those of the initial 1D-O polymer spectrum. The same transformation was observed for other specimens of the 1D-O polymer at any applied initial pressure in a number of other series of the high-pressure Raman measurements. We have not been able to find the threshold pressure for this transformation: it occurs at pressure even as small as 0.32 GPa. The Raman spectrum taken at 0.32 GPa in Fig. 1b demonstrates the identity of the transformed 1D-O polymer as follows from the detailed analysis of the Raman features.
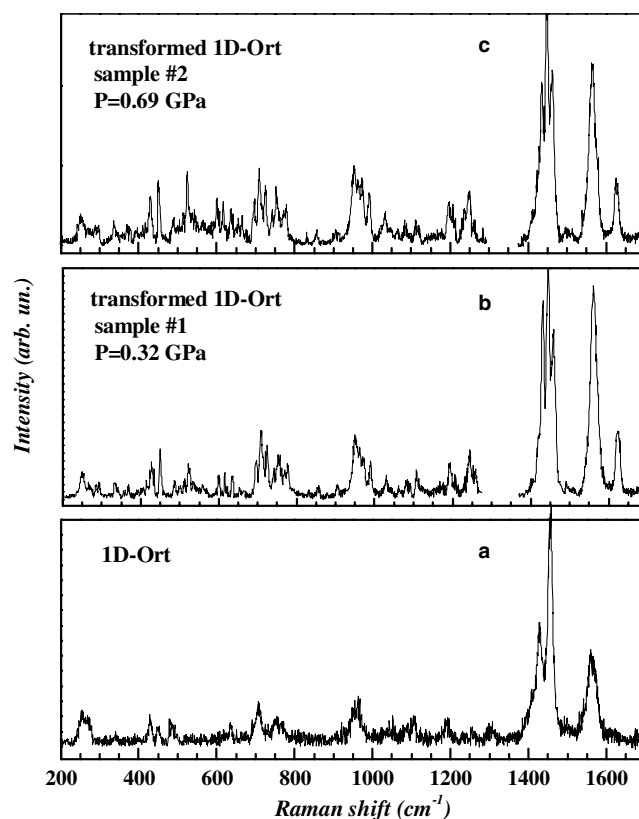

Fig. 1. Raman spectrum of the initial orthorhombic phase based on 1D-O polymers of C_{60} at normal conditions (a) and the spectrum of the same sample at 0.69 GPa (c). Another specimen shows the same transformation of the Raman spectrum at 0.32 GPa (b).

Fig. 2 shows the Raman spectrum of the transformed 1D-O polymer as compared with the Raman spectra of the planar 2D-R and 2D-T polymeric phases. The comparison of the Raman spectra of the transformed 1D(O)-polymer (Fig. 2a), to those of the 2D(T) (Fig. 2c) and 2D(R) (Fig. 2b) polymers shows their differences in the number of peaks, their positions and relative intensities. The in-
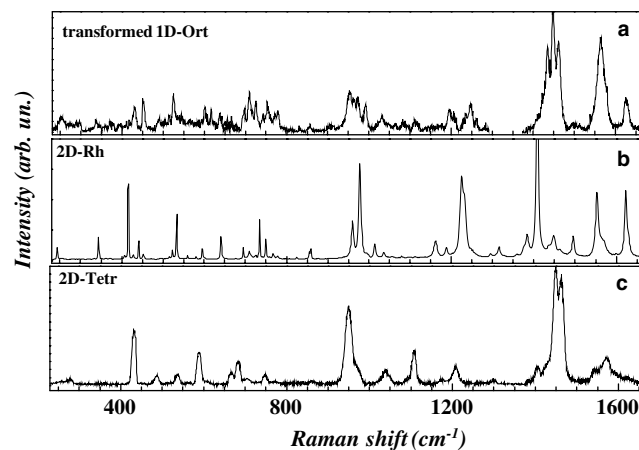

Fig. 2. Raman spectra of the transformed orthorhombic phase (a) and the rhombohedral (b) and tetragonal (c) phases based on various planar polymers of C_{60} (2D-T and 2D-R polymers).

Table 1
The phonon frequencies for the 2D-R, 2D-T, 1D-O and transformed 1D-O polymeric phase of C_{60}

2D-R polymer [14]		2D-T polymer [15]		1D-O transformed polymer [d]		1D-O polymer [d]		Monomeric C_{60} [16]	
Mode[a]	ω_i (cm^{-1})	Mode[b]	ω_i (cm^{-1})	Mode[e]	ω_i (cm^{-1})	Mode[c]	ω_i (cm^{-1})	Mode	ω_i (cm^{-1})
$H_g(1)$	245	$H_g(1)$	259		248	$H_g(1)$	251	$H_g(1)$	273
$H_g(1)$	267		280		266		270		
$H_g(1)$	308				288				
$H_u(1)$	342				333		340		
$F_{2u}(1)$	366				366				
					389				
$G_u(1)$	406								
$H_g(2)$	415				411				
$H_g(2)$	438	$H_g(2)$	431		427	$H_g(2)$	425	$H_g(2)$	437
$H_g(2)$	451						450		
$A_g(1)$	492	$A_g(1)$	481		484	$A_g(1)$	486	$A_g(1)$	496
$F_{1u}(1)$	520				521	$\Omega(x)$	523		
$F_{2g}(1)$	532	$F_{2g}(1)$	536		527				
$F_{1g}(1)$	558	$F_{1g}(1)$	563		561				
$H_u(2)$	579	$F_{1g}(1)$	588						
$H_u(2)$	596				598				
		$\Omega(x)$	610		614				
$H_u(3)$	640				634	$H_g(3)$	635		
					654				
		$H_g(3)$	666		662				
$H_g(3)$	695				694				
$F_{2u}(2)$	709				707		707	$H_g(3)$	710
$H_g(3)$	712				722				
$H_g(3)$	731				739				
$H_g(4)$	749	$H_g(4)$	747		752	$H_g(4)$	752		
$F_{2g}(2)$	767								
$H_g(4)$	776		772		774		769	$H_g(4)$	774
$F_{2u}(3)$	827								
$H_u(4)$	856				853	$\Omega(x)$	843		
$H_u(4)$	868	$\Omega(x)$	864						
					903	$\Omega(x)$	897		
$G_g(2)$	958	$G_g(2)$	951		947	$\Omega(x)$	957		
					959				
$F_{1g}(2)$	977	$F_{1g}(2)$	970		969				
					987				
$F_{2u}(4)$	1016								
$F_{2u}(4)$	1037				1027	$\Omega(x)$	1034		
$H_g(5)$	1042	$\Omega(x)$	1041						
$H_g(5)$	1078	$H_g(5)$	1090		1082	$H_g(5)$	1082		
$H_g(5)$	1109		1107		1105		1105	$H_g(5)$	1100
$G_g(3)$	1158	$G_g(3)$	1176						
$G_g(3)$	1195				1190		1190		
$F_{2g}(3)$	1204	$F_{2g}(3)$	1206		1205				
$H_g(6)$	1224								
$H_g(6)$	1230				1241	$H_g(6)$	1240	$H_g(6)$	1243
$H_g(6)$	1260				1257		1258		
$G_g(4)$	1314	$G_g(4)$	1299				1307		
$H_g(7)$	1385	$H_g(7)$	1404		1386	$H_g(7)$	1398		
$A_g(2)$	1410				1423		1416		
			1428		1429		1430	$H_g(7)$	1428
		$A_g(2)$	1447		1442		1442		
		$F_{1g}(3)$	1463		1455	$A_g(2)$	1457	$A_g(2)$	1470
$F_{1g}(3)$	1495								
$H_g(8)$	1554	$F_{2g}(4)$	1543		1559				
$H_g(8)$	1563	$H_g(8)$	1567		1559	$H_g(7)$	1560		
$H_g(8)$	1569	$G_g(6)$	1598				1575	$H_g(8)$	1575
$G_g(6)$	1621				1621		1621		
$G_g(6)$	1627								

The corresponding values for monomeric C_{60} are also included.

[a] The peak positions and mode assignment for the 2D-R polymeric phase refers to the irreducible representations of the C_{60} molecule and follows in general that of [3].

[b] The mode assignment or the 2D-T polymeric phase follows that in [3]. The modes marked by $\Omega(x)$ have unclear assignment.

[c] The mode assignment or the 1D-O polymeric phase follows that in [17].

[d] Data related to present work.

[e] No assignment can be made.

crease of the number of peaks testifies that the point symmetry of the C_{60} cage in the new phase is lower than in the pristine orthorhombic polymer (symmetry D_{2h}). In the case of the cross-linking of the pristine orthorhombic polymer the lowering of symmetry can be associated with the formation of new inter-cage covalent bonds between the C_{60} clusters that belong to the neighbouring polymeric chains in the structure of the orthorhombic phase. The distinction of the Raman spectrum of the transformed 1D(O)-polymer and those of the 2D polymerized tetragonal and rhombohedral phases of C_{60} may be indicating that the novel chemical bonds in the transformed orthorhombic phase are not the typical $[2+2]$ cycloaddition bonds but rather single bonds between polymeric chains. Note that this process, which can give rise to the formation of both the 2D and 3D polymeric structures of C_{60}, must be accompanied by a re-distribution of the positions of the single and double bonds into the C_{60} clusters. The detailed data related to the Raman mode frequencies of these polymeric phases, as well as the Raman frequencies and the mode assignment of the pristine C_{60} are summarized in Table 1. The in situ Raman data obtained in the present work confirm that the 1D-O polymer undergoes an irreversible transformation to a new phase by the application of pressure even as small as 0.32 GPa.

To study the structural aspects of the observed transformation we have compared the X-ray diffraction pattern of the initial 1D-O polymer at normal conditions with those of the high pressure-treated 1D-O polymer after pressure release. The pressure was raised up to 3 GPa at 20 °C while the duration of treatment was 10 min. The X-ray diffraction pattern of the initial 1D-O polymer at normal conditions and the diffraction pattern of the pressure-treated 1D-O polymer after pressure release are shown in Fig. 3a,b, respectively. The inset in Fig. 3b shows the Raman spectrum of the pressure-trea-

ted 1D-O polymer taken after pressure release at normal conditions. As shown in Fig. 3a,b there are no significant differences in the X-ray diffraction patterns of the 1D-O polymer before and after pressure treatment. The positions of all observed peaks are the same, while small difference in peak intensities may be related to the powder material preparation. In addition, the ex situ Raman spectrum of the pressure-treated 1D-O polymer taken after pressure release is the same with the spectrum of the initial polymer. The fact, that the ex situ X-ray and Raman data of the high-pressure treated 1D-O polymers do not show any changes in the crystal structure and phonon spectrum of the material, contrary to the transformation clearly shown in the in situ high-pressure Raman study, implies that these changes are related to the laser irradiation of the samples along with the high pressure application taking place during the in situ high-pressure Raman measurements. Therefore, the crucial role of the sample irradiation under high pressure for this transition to happen, indicates that the transformation observed in the in situ Raman study is associated with pressure-assisted photoinduced polymerization of the linear 1D-O polymer. Moreover, it is important to note that at ambient conditions the 1D-O polymer is stable under light irradiation and no photoinduced polymerization was observed at moderate laser power, further increase of the laser power leads to overheating of the sample, which results in the destruction of the polymer. As for the possible mechanism of the high pressure photoinduced transformation of the linear orthorhombic polymeric phase of C_{60}, one can speculate that it may be similar to the recently reported high pressure photoinduced transformation of crystalline benzene [18]. The stimulating influence of the laser irradiation on the benzene transformation at high pressures was associated to the excitation of the molecular electronic states from the basic S_0 state to the first S_1 excited state.

In conclusion, the transformation of the Raman spectrum of the 1D-O polymer of C_{60} by the application of external pressure may be attributed to the pressure-assisted photo-polymerization. This polymerization may be accomplished by covalent bond formation between molecules belonging to adjacent polymeric chains resulting in the formation of the new 2D or 3D polymerized state of C_{60}. The unambiguous determination of the structural properties of the new phase needs further experimental and theoretical investigations.
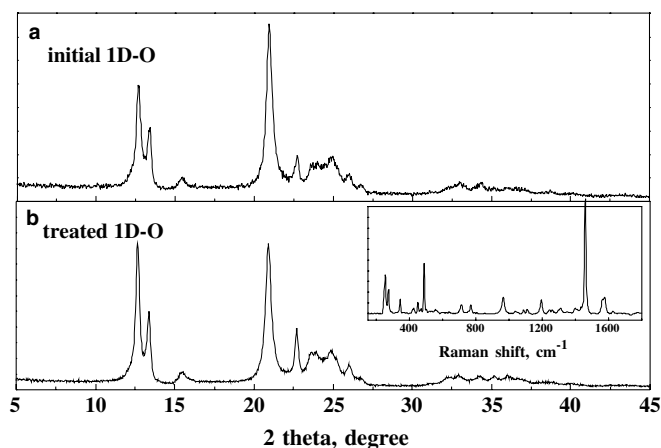
Acknowledgements

Fig. 3. X-ray diffraction pattern of the initial orthorhombic phase of C_{60} at normal conditions (a), X-ray diffraction pattern of the pressure-treated orthorombic phase after pressure release (b). (Inset) Raman spectrum of the pressure-treated orthorhombic phase after pressure release.

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