C 70 in Benzene, Hexane, and Toluene Solutions

2 **AUTHORS**, INCLUDING:

Alexandr V Talyzin
Umeå University
126 PUBLICATIONS **1,480** CITATIONS

C$_{70}$ in Benzene, Hexane, and Toluene Solutions

A. V. Talyzin* and I. Engström

Ångström Laboratory, Inorganic Chemistry, Box 538, SE-751 21, Uppsala, Sweden

Received: March 17, 1998; In Final Form: May 18, 1998

The structural transformations of the C$_{70}$ in benzene, toluene, and hexane solutions were studied. The X-ray powder diffraction experiments made directly on the C$_{70}$ solution samples showed structural transformations of similar types for all the tested solvents. It is shown that C$_{70}$ in benzene and hexane solution forms solvated phases at room temperature similar to the toluene solvate described before (Agafonov, V.; Ceolin, R.; Andre, D.; De Bruijn, J.; Gonthier-Vassal, A.; Szwarc, H.; Rodier, N.; Dugue, J.; Toscani, S.; Sizaret, P. Y.; Fabre, C.; Greugny, V.; Rassat, A. *Chem. Phys. Lett.* **1993**, *208*, 68). Experiments with C$_{70}$ crystallized from benzene solutions performed at room temperature resulted in the formation of the orthorhombic solvated phase, while crystals grown at $T > 40$ °C appeared to be a mixture of the pure C$_{70}$ hcp phase and the monoclinic solvate phase.

1. Introduction

It is known that C$_{60}$ forms solvates with a number of different organic solvents. Ruoff et al.[2] reported that the temperature dependence of solubility has its maximum near room temperature for several solvents. Smith et al.[3] showed that this anomalous behavior of the solubility can be explained thermodynamically. According to their model, two phases can exist in equilibrium with solution, one of them with a positive enthalpy of dissolution, another with a negative. These phases can either be both solvated with different amounts of solvent or one of them can be pure C$_{60}$. Usually at room temperature, the solvate is stable in the solution. At some temperature a phase transition between the two forms occurs. The solvated crystal melts and another phase forms: pure C$_{60}$ or C$_{60}$ with a lesser amount of solvent. This phase transition gives a change in the slope of the temperature dependence of solubility. Differential scanning calorimetric experiments made for a number of solvents[4−6] showed that such transitions are detected as a maximum in the temperature dependence of the heat capacity. This model is confirmed by the results of direct observations of the phase transition C$_{60}$−C$_{60}$·4C$_6$H$_6$ in benzene.[7]

On the whole, the picture of the C$_{60}$ behavior in solution looks more or less clear, while only very little information is available for the C$_{70}$ phases and its solvates formed by crystallization from different solutions. The only work reported so far for C$_{70}$ solvates obtained by evaporation of toluene solution at room temperature is by Agafonov et al.[1] These authors suggest a C$_{70}$−toluene solvate of 1:1 composition and orthorhombic structure. On the other hand, Valsakumar et al.[8] reported a pure C$_{70}$ hcp structure obtained by evaporation of toluene solution at 110 °C. They suggested the difference in the growth temperature as a reason they did not obtain the solvated structure found in ref 1. According to this suggestion we would expect the existence of a phase transition similar to the one known for the C$_{60}$ solvates. But it appears that the solubility of C$_{70}$ does not have a maximum in the whole temperature range where the toluene exists as a liquid,[9] and no anomalies were found in the C$_{70}$-toluene system by calorimetric methods.[10]

Even less is known about the C$_{70}$ behavior in other solvents. Large C$_{70}$ crystals were obtained by crystallization from benzene

solution,[11] but no structural analysis was performed on these crystals. These crystals remain stable even after several hours of heating at $T = 200$ °C, while solvates reported for toluene decomposed at 110−140 °C by the solvent loss.[1]

It is questionable if any other solvates of C$_{70}$ exists in various solvents, if they have similar structures as those of the C$_{60}$ solvates, if any phase transitions between solvates exist, if it is possible to grow pure C$_{70}$ crystals from solution, and if so, under which conditions.

Here we present the results of the investigations of C$_{70}$ crystallization from a benzene solution. The behavior of C$_{70}$ in benzene, hexane, and toluene studied by X-ray diffraction methods directly in solution is compared and discussed.

2. Experimental Section

All experiments were performed with C$_{70}$ of 99% purity (MER corporation). The crystals were grown from a benzene solution by slow evaporation (1−2 mL per day). The growth methods are described in detail in our previous publications.[12] Briefly, the growth device consists of two chambers separated by a filter. The lower chamber is heated from the bottom, the solvent evaporated from the lower chamber is condensed on the walls of the upper chamber, which has a lower temperature. After condensation on the walls of the upper chamber takes place, the solvent flows down to a filter where the source fullerene powder is situated. The solvent dissolves a part of this powder and then drops back to the lower chamber. The rate of the solvent circulation is regulated by the difference in the temperatures of the lower and upper chambers. This method allows the use of very small amounts of solvent (10−15 mL) for the growth of several millimeter size crystals. Crystallization can be performed at different temperatures without the loss of solvent and the pollution of the environment.

The powder samples obtained by the crystallization procedure were studied by X-ray diffraction methods with the Siemens D5000 diffractometer. Silicon was used as internal standard in all experiments. For the investigation of C$_{70}$ powder directly in solution, a special kind of sample was used: the powder was placed between two thin glass plates in a drop of solvent. To prevent evaporation of the solvent, the glasses were glued

together by the silicate glue. A flat cell of this kind (0.1−0.3 mm thick) was studied immediately after preparation. However, a good X-ray powder pattern of the sample of this kind could not be obtained in a D5000 diffractometer. Therefore, a Siemens system consisting of a Smart CCD area detector and a direct-drive rotating anode as an X-ray generator was used. The radiation was Mo Kα (tube voltage 50 kV, tube current 24 mA, cathode gun 0.1 × 1 mm) monochromatized by using an incident beam graphite monochromator and by passing it through a collimator of 0.5 mm diameter to the sample. The diffracted X-rays were collected on a detector 512 × 512 pixels in area. By this method, a large portion of the Debye ring at different 2θ settings could be measured, and the method is sensitive enough to give powder patterns even for samples placed between two glass plates and filled with the solution. By this method, the transformations of C_{70} powder under the influence of different solvents could be measured, and the heating experimental setup also made it possible to observe the phase transitions occurring in C_{70}−solution system. The same technique was used for the investigation of the C_{60}.[7]

3. Results and Discussion

3.1. Results of the Crystallization Experiments from a Benzene Solution. Crystallization experiments were performed for the C_{70}−benzene system. To get a better quality of the crystals a slow growth rate was used. An experiment usually continued for 4−6 weeks. Several experiments were performed at different temperatures resulting in crystals of different morphologies.

(a) The first group of experiments was made at temperatures $T < 40$ °C. The resulting residue consisted of large black platelets of rectangular shape (with a size up to 3 × 2 mm^2) and polycrystalline powder which consisted of a mixture of small rectangular platelets and rhombic-shaped red platelets. Some of the rectangular platelets have also the shape of flat pyramids.

These crystals are stable in air. After several months exposure at ambient conditions, they showed no change in the X-ray powder pattern. The pattern was compared with all known structures reported and predicted for C_{70}, but none gave a satisfactory agreement. The X-ray powder studies combined with single-crystal methods (Laue and oscillation pictures taken from different orientations) showed that a crystal grown from benzene solution at 35−40 °C has an orthorhombic structure very similar to the structures of the toluene solvated phase described before. Cell parameters refined for different powder samples are similar to the toluene-solvated structure, but remarkably changed from one sample to another.

It was found that the quality of the measured pattern strongly depend on the method of sample preparation. When initial intergrown crystallites were crushed very gently, only by pressing, without rotation, a good pattern was obtained (see Figure 1, curve 1). If pressing combined with rotation was used, the intensity of the peaks considerably decreased. The diffraction lines became wide and badly resolved. (Figure 1, curve 2). This is the reason for a change in the cell parameters when a different samples were used. For example, a sample prepared from small intergrown crystallites gives $a = 21.47$ Å, $b = 32.71$ Å, $c = 10.80$ Å, and $V = 7590$ Å^3 (Table 1), while the sample prepared from large platelets by very gentle crushing gives $a = 20.99$ Å, $b = 32.85$ Å, $c = 11.01$ Å, $V = 7.596$ Å^3 ($a = 21.075$, $b = 32.99$, $c = 10.84$ Å, and $V = 7540$ Å^3 by the data for toluene solvate, Agafonov et al.[1]) It is known that crushing of pure C_{70} produces stacking faults, but in the our case it can
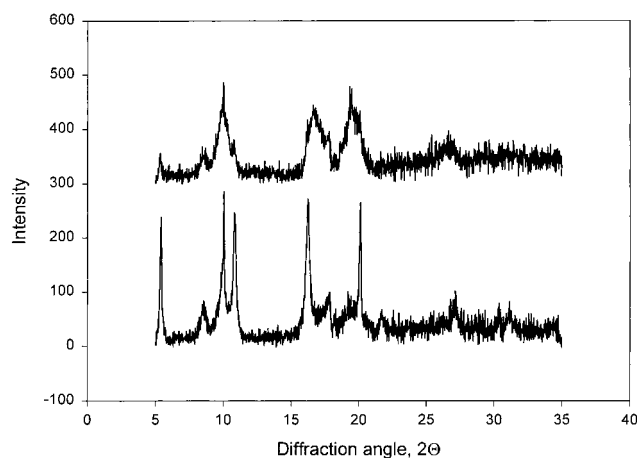

Figure 1. X-ray powder patterns for the C_{70} sample crashed very gently, only by pressing (curve 1), and for sample crushed with rotation (curve 2).

TABLE 1: X-ray Powder Diffraction Data for C_{70}−Benzene Solvate (Cu Kα$_1$). Well Resolved Reflections with High Intensity Are Listed

d (Å)	hkl	I
16.43	020	67
10.17	210	38
9.24	111	31
9.01	021	53
8.17	040	55
5.44	060	73
5.39	002	72
5.17	112	47
4.97	251	95
4.87	061	55
4.82	202	54
4.76	411	59
4.69	070	82
4.56	170	80
4.41	142	100
4.30	302	29
4.21	171	31
3.09	333	13

TABLE 2: X-ray Powder Diffraction Data for Starting C_{70} Obtained by Siemens D5000 and Siemens Smart System Diffractometers Compared with C_{70} Solvates in Benzene, Toluene, and Hexane Solutions

Siemens D5000					
d-spacing	structure	SSS	benzene	toluene	hexane
			10.347	10.01	9.985
9.189	002 hcp		9.013	9.142	8.964
8.69	010 hcp	8.645			
8.091	011 hcp				
5.295	110 hcp		5.266	5.420	
5.084	110 rh	5.143	4.945	4.953	5.068
4.889	013 hcp				
4.510	112 hcp				
4.461	113 rh	4.457	4.628	4.575	4.521
4.293	201 rh			4.389	

be complicated by partial loss of solvent during the crushing. The single-crystal methods showed that it is typical for these crystals to have extremely bad packing along the b direction. No parameter value be obtained from oscillation picture along this direction because of multitwinning and stacking faults, but oscillation along a and c directions gives the values $a = 21.00$ Å, and $c = 10.8$ Å.

The main face of platelets usually shows reflections of several orders from the (oko) planes with typical d/n-spacing values of about 32.8 Å.
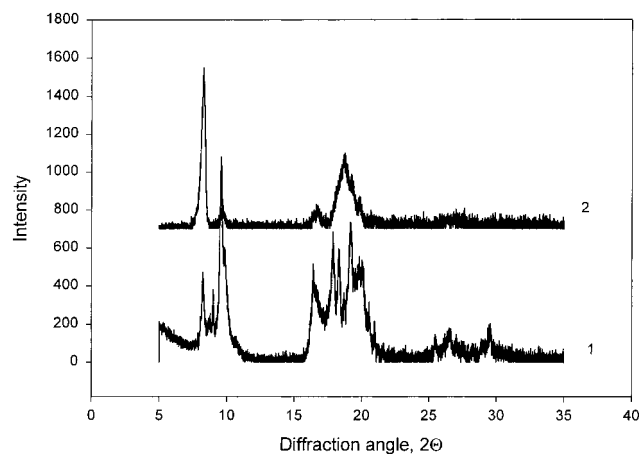
C$_{70}$ in Benzene, Hexane and Toluene Solutions

J. Phys. Chem. B, Vol. 102, No. 34, 1998 **6479**

Figure 2. X-ray powder patterns of C$_{70}$ samples grown at 340 K with evaporation rate: (1) 2 mL per day, (2) 10 mL per day.

Figure 3. X-ray powder patterns for C$_{70}$ samples: (1) starting powder provided by MER corporation, (2) crushed crystals grown from benzene solution, and (3) sample 2 after heat treatment.

(b) $T > 40$ °C The same growth procedure gave crystals and intergrown crystallites of near-hexagonal habitus. Single-crystals with smooth well-formed faces and sizes up to $0.5 \times 0.2 \times 0.2$ mm^3 were obtained. While some of the crystals have hexagonal morphology, others look like deformed hexagonal prisms. The powder sample was prepared by crushing of collection of intergrown crystallites and investigated by powder X-ray diffractometry.

It was found that the quality of the diffraction patterns strongly depend on the crystallization conditions. A comparison of two powder samples, one grown with the rate of evaporation of 10 mL per day and the other with the rate of 2 mL per day, is shown on the Figure 2, curves 1 and 2, respectively. The slowly grown sample produced more peaks and better sharpness than the sample grown rapidly.

While analyzing patterns, we took into account that crystals have near hexagonal morphology. After analysis, we suggest that the X-ray patterns can be described as a mixture of the minor hcpI phase with cell parameters $a = 10.17$ Å, $c = 18.52$ Å, and as a main phase monoclinic structure with cell parameters $a = 9.89$ Å, $b = 10.76$ Å, $c = 37.44$ Å, and $\gamma = 120°$, which can be described as a distorted hcp. The same as for the crystals grown at room temperatures a difference in parameters a, b, and c, in a range 0.2 Å was observed for different samples. The c parameter of this structure is about twice the value of the c parameter of the hcpI phase. The monoclinic phase is suggested to be a distorted hcpI phase with a doubled c parameter. The degree of distortion and amount of solvent incorporated to the structure probably depends on a rate of growth. It could explain the difference between powder samples grown with low and high evaporation rate.

3.2. Heating Experiments. To check our suggestion about solvated nature of grown crystals we performed a heating experiments with Siemens Smart System (SSS) diffractometer. The heating experiments in argon flow were made on the powder prepared from crystals grown at 35 and 65 °C with very similar result. The X-ray patterns were recorded with a step of 10 °C and 15 min time of exposure. The results showed that these phases are stable up to 140 °C. At this temperature the phase transition occurs. Initial lines of the room temperature phase consist of a number of individual diffraction spots due to the relatively large size of grains. At 140 °C, all spots disappear and regular lines of C$_{70}$ hcp phase without any spots are observed. To define the nature of this phase transition, we performed thermogravimetric experiments. Two samples were analyzed: one made of crushed crystals grown at room
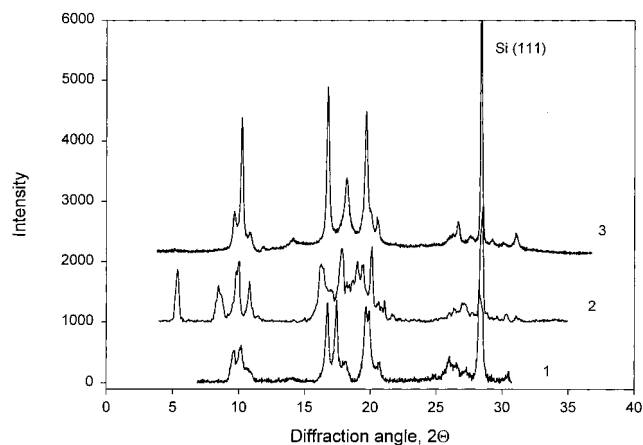
temperature and the other on crushed crystals grown at 65 °C. The results were similar for both samples. A slow mass loss started at 90 °C, the sharp anomaly at 140–150 and then slow mass loss continued up to 300 °C with total mass loss of 15% for the first sample and 11% for the second. The temperature of this transition and the amounts of the mass losses are very close the data of Agafonov et al.[8] for C$_{70}$–toluene solvate.

A more detailed X-ray diffraction pattern was recorded with D5000 diffractometer on a sample which was used for the thermogravimeric experiments (Figure 3, curve 3). In contra-distinction to the data of Agafonov et al.,[1] who observed only a few peaks for a similar sample heated to 250 °C, the quality of the pattern obtained on our sample is rather good. It can be explained in terms of a mixture of fcc ($a = 14.93$ Å) and hcp ($a = 10.57$ Å and $c = 17.27$ Å). These data are in a good agreement with the data reported for pure C$_{70}$, Vaughnan et al.[13]

In a rough outline, the phases in system C$_{70}$–benzene look similar to the phases of the C$_{70}$–toluene system. At room temperature solvated phases were obtained for toluene grown samples, while a temperature of 110 °C gave rise to the formation of hcp crystals.

Our experiments showed a similar picture for benzene: the solvated phase exists at room conditions with the same orthorhombic cell and with very similar cell parameters as for those crystals grown from toluene, as well as for the hcp phase in a mixture with deformed hcp at higher temperatures.

3.3. In Situ X-ray Powder Diffraction Experiments. The next step of our studies was to perform experiments similar to those described in the previous publication.[7] In that work, we observed the C$_{60}$ behavior in benzene. We found that the source C$_{60}$ material placed in benzene solution transformed to new crystals of solvated phase by slow recrystallization from fcc pure C$_{60}$ to solvated phase C$_{60}$·4C$_6$H$_6$. Upon heating of a powder filled by saturated solution the phase transition from a solvated phase to pure C$_{60}$ was observed both by visual observations and X-ray diffraction method. On the basis of the results of our crystallization experiments we expected to find similar behavior in the system C$_{70}$–benzene.

The main problem in those kind of measurements appears to be a low resolution of the SSS diffractometer with our samples. To compare quality of spectra, the same powder sample of pure C$_{70}$ was studied on two diffractometers: Siemens D5000 with reflected beam scheme and SSS diffractometer with transmitted beam scheme.
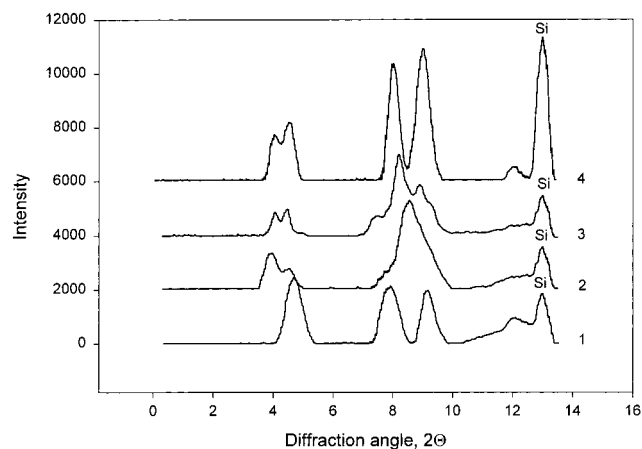
Figure 4. X-ray powder paterns for samples: (1) starting C_{70} powder, (2) C_{70} in the benzene solution, (3) C_{70} in a toluene solution, (4) C_{70} in a hexane solution.

The difference can be observed on Figure 3, curve 1, and Figure 4, curve 1 and d spacing values given in Table 1. It is clearly seen that the resolution became much worse in the second case. Because no good X-ray patterns were obtained in Siemens D5000 for the cells filled by solution, we had to use more powerful instrument but with worse resolution. In that case, only qualitative conclusions can be made because of small number of well resolved lines.

X-ray powder analysis of the initial C_{70} powder as was obtained from MER Corporation (Figure 3, curve 1) shows it to be a mixture of HcpII phase with the cell parameters, $a = 10.57$ Å and $c = 17.33$ Å, and the rhombohedral phase with $a = 10.13$ Å and $c = 27.77$ Å. These are in good agreement with data reported for the room-temperature phases.[13]

According to the information provided by the MER Corporation the powder was obtained by evaporation of C_{70} solution in toluene and heated several hours at 200 °C to remove solvent traces.

After the source C_{70} powder was filled by the solution, we did not observe any changes in morphology of grains, and no new crystallites formed. It was the same for samples stored both at room temperature and at 7 °C for several weeks. The X-ray powder analysis showed that changes took place in the structure of grains without changes in morphology.

The same experiments were made for benzene, toluene, and hexane solution and the resulting patterns are shown on Figure 4. The changes of the C_{70} pattern were similar for all three solvents, but in the case of benzene and toluene these changes were very fast, less than 30 min, while the pattern of C_{70} in hexane came to equilibrium only after 2 h. The solubility of C_{70} in hexane is about 100 times less than the solubility in toluene and benzene, and it is logical to suggest that processes of interaction should be slower in the C_{70} hexane system. The d spacing data of observed lines are listed in Table 1. The changes in the X-ray powder diffraction patterns appear to be reversible upon drying of the samples. It took several days at room temperature conditions to return back to the pure C_{70} patterns for all three solvents.

The heating experiments from room temperature to the temperature close to the boiling point were carried out for all three solvents. In contradistinction to the expected analogy with C_{60} system, no changes were found in the X-ray patterns.

These data are in agreement with the data on solubility dependence of C_{70} and calorimetric measurements according to which no anomalies were found in those systems. On the other hand, crystallization experiments showed that there are some certain structural changes in crystals grown at different temperatures both for toluene[1,8] and benzene.

It is clear that solvates of C_{70} are very different from C_{60} solvates and have properties more similar to pure C_{70}. Relatively small amounts of solvent incorporated to structure gives more stability and a density of the solvated phase very similar to the density of pure C_{70}.

C_{60} solvates formed by recrystallization from fcc phase grains to newly formed crystals, while C_{70} transforms by incorporating of solvent to source grains without change in morphology. The fact that the phase transition can be observed only by crystallization experiments and is not observed by other methods probably could be explained by a rather small difference in chemical potentials between solvated and nonsolvated phases. In that case only the crystallization in conditions close to equilibrium could produce different phases and the field of metastable existence of phases should be large.

4. Conclusion

In conclusion, it is shown that the solid C_{70} in benzene and hexane solutions transforms to solvated phases very similar to the toluene solvate described before. In contradistinction to the C_{60} behavior in solutions, the process of C_{70} transformation from a C_{70} powder to solvated phase occurs without formation of new macroscopic crystallites and without any visual morphological changes in the shape of grains.

No phase transitions were found by the heating experiments for all three solvents in the temperature range from room temperature to the solvent boiling point. Nevertheless, the powder X-ray diffraction pattern showed that different phases were obtained by the crystallization from a solution in a benzene at temperatures $T < 40$ °C and at $T > 40$ °C. X-ray powder diffraction analysis showed an orthorhombic structure for low-temperature phase and a mixture of a monoclinic phase together with pure hcpI phase for high temperature. The composition of the two C_{70}−benzene solvates is proposed to be 1:1 according to thermogravimetrical experiments.

References and Notes

(1) Agafonov, V.; Ceolin, R.; Andre, D.; De Bruijn, J.; Gonthier-Vassal, A.; Szwarc, H.; Rodier, N.; Dugue, J.; Toscani, S.; Sizaret, P. Y.; Fabre, C.; Greugny, V.; Rassat, A. *Chem. Phys. Lett.* **1993**, *208*, 68.

(2) Ruoff, R. S.; Malhotra, R.; Huestus, D. L.; Tse, D. S.; Lorents, D. C. *Nature*, **1993**, *362*, 140.

(3) Smith, A. L.; Li, D.; King, B.; Zimmerman, G. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society Proceeding Series, PV 94−24; Pennington, NJ, 1994; p 443.

(4) Smith, A. L.; Walter, E.; Korobov, M. V.; Gurvich, O. L. *J. Phys. Chem.* **1996**, *100*, 6775.

(5) Olofsson, G.; Wadso, I.; Ruoff, R. S. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society Proceeding Series PV 96−10; Pennington, NJ, 1996; p 17.

(6) Korobov, M. V.; Mirakyan, A. L.; Avramenko, N. V.; Odinec, I. L.; Ruoff, R. S. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society Proceeding Series PV 96−10; Pennington, NJ, 1996; p 5.

(7) Smith, A. L.; Strawhecker, K.; Shirazi, H.; Olofsson, G.; Wadso, I.; Qvarnstrom, E. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society Proceeding Series; Pennington, NJ, 1997; Vol. 4.

C$_{70}$ in Benzene, Hexane and Toluene Solutions

J. Phys. Chem. B, Vol. 102, No. 34, 1998 **6481**

(8) Talyzin, A. V. *J. Phys. Chem. B.* **1997**, *101*, 9679.

(9) Valsakumar, M. C.; Subramanian, N.; Yousuf, M.; Sahu, P. Ch.; Hariharan, Y.; Bharati, A.; Sankara Sastry, V.; Janaki, J.; Rao, G. V. N.; Radhakrishnan, T. S.; Sundar, C. S. *Phys. Rev. B* **1993**, *48*, 9080.

(10) Zhou, X.; Liu, J.; Jin, Z.; Gu, Z.; Wu, Y.; Sun, Y. *Fullerene Sci. Technol.* **1997**, 5 (1), 285.

(11) Korobov, M. V.; Mirakyan, A. L.; Avramenko, N. V.; Neretin, I. S.; Stukalin, E. B.; Ruoff, R. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Electrochemical Society Proce4eding Series 97-14; Pennington, NJ, 1997; Vol. 4, p 540.

(12) Sekine, T.; Kuoe, H.; Makimura, C.; Tanokura, Y.; Takeuchi, T.; *Synth. Met.* **1995**, *70*, 1383. Talyzin, A. V.; Ratnicov, V. V.; Syrnicov, P. P. *Phys. Solid State* **1996**, *7*, 1531.

(13) Vaughnan, G. B. M.; Heiney, P. A.; Fischer, J. E.; Luzzi, D. E.; Ricketts-Foot, D. A.; McGhie, A. R.;Yiu-Wing-Hui; Smith, A. L.; Cox, D. E.; Romanow, W. J.; Allen, B. H.; Coustel, N.; McCauley, J. P.; Smith, A. M., III *Science*, **1991**, *254*, 1350.