Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 350–352
Mendeleev Communications

New hybrid nanostructures of C_{60} fullerene based on an amphiphilic copolymer of *N*-vinylpyrrolidone and (di)methacrylates

Svetlana V. Kurmaz* and Nadezhda A. Obraztsova

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: skurmaz@icp.ac.ru

DOI: 10.1016/j.mencom.2015.09.011

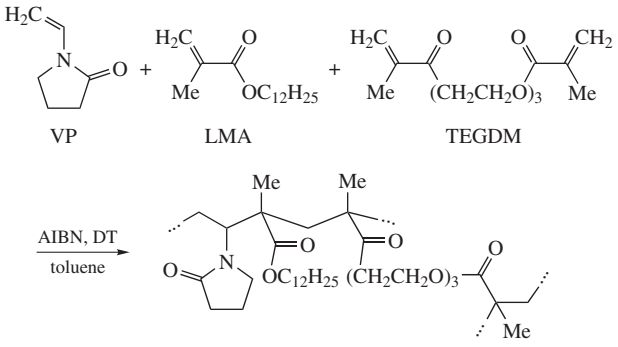
New hybrid macromolecular nanostructures of C_{60} fullerene based on an amphiphilic copolymer of *N*-vinylpyrrolidone with lauryl methacrylate and triethylene glycol dimethacrylate were prepared in isopropyl alcohol.

To prepare stable C_{60} hybrid macromolecular structures (HMMS) or inclusion complexes, supramolecular chemistry approaches based on spontaneous aggregation of polymer colloids, *i.e.*, micelles, emulsions in polar solvents are widely used. For this, amphiphilic block copolymers of linear structure forming polymer micelles in appropriate solvents are typically applied.[1] Thereby, stable structures were produced by the mixing of polymer colloids in polar solvents and those of C_{60} in toluene.[2–7] It allows one to convert C_{60} into water-soluble colloids for biomedical applications like its low molecular weight derivatives.[8]

Recently, we found that the amphiphilic copolymers of *N*-vinylpyrrolidone (VP) and triethylene glycol dimethacrylate (TEGDM) of a branched type were self-organized in isopropanol and water to obtain macromolecular host–guest inclusion complexes promising for biomedical applications.[9,10]

On the mixing of micellar solutions with a toluene solution of the fullerene, polymer colloids and C_{60} spontaneously assembled into stable colloidal nanocomposites.[3] Moreover, polymers containing electron-donor oxygen and nitrogen atoms can associate into charge-transfer complexes with the fullerene.[3,7] The aim of this study was to produce the stable hybrid macromolecular nanostructures of C_{60} fullerene using the amphiphilic VP–LMA–TEGDM terpolymer in isopropyl alcohol and to examine their formation depending on the copolymer structure solution given by the copolymer concentration, and on a copolymer : fullerene ratio in solution.

The VP–LMA–TEGDM terpolymer† was prepared by radical copolymerization of VP, LMA and TEGDM in toluene in the presence of a chain transfer agent (Scheme 1) as described previously.[12,13] Dimethacrylate was a branching agent. One of TEGDM double bonds participates to grow the copolymer backbone, and the pendant second one involves into side reactions. The branch points appeared when the pendant C=C bonds react with another primary chain. The chain transfer agent 1-decanethiol (DT) restricted the uncontrolled growth of polymeric chains to avoid network formation. At chosen TEGDM and DT ratios, the soluble copolymer in polar and low-polar solvents was produced.



Scheme 1

After the copolymerization, the high molecular weight copolymer was isolated from the mixture by hexane as a precipitant. The low molecular weight copolymer stayed in hexane. After removal of the solvent, we obtained ternary copolymer. According to IR and ^{1}H NMR data,‡ it contained significantly more hydrophobic units LMA than high molecular weight product. This copolymer was used in this study as the most suitable for self-organization in a polar solvent.

The absorption band at 724 cm^{-1} related to the rocking vibrations of CH_2 groups in long chain alkyl substituent of LMA units is observed in the IR spectrum of the copolymer. Intense proton signals of CH_2 groups of the alkyl substituent LMA units were recorded in the ^{1}H NMR spectrum at δ 1.64–1.65 ppm. The IR spectrum contains strong and characteristic absorption bands at 1724 and 1672 cm^{-1} related to the stretching vibrations of C=O groups of TEGDM and VP units, respectively. Two groups of proton signals were observed in the ^{1}H NMR spectrum of the copolymer. The first set includes the signals of NCH_α protons in the polymer chain and the $–CH_2C=O$ fragments of pyrrolidone at δ 3.0–4.0 ppm. The second one relates to the signals of CH_2 protons in the polymer chain and of the CCH_2C and NCH_2 fragments of pyrrolidone at δ 1.4–2.4 ppm.[14] The proton signals of Me group were detected at δ 0.9, 0.91 and 0.93 ppm.

The molecular weight of the copolymer was determined by GPC with refractometric (RI) and light scattering (MALLS) detectors.[13] The copolymer molecular weights were M_n = = 2.0×10^3, M_w = 9.9×10^3 or M_n = 6.2×10^3, M_w = 37.4×10^3,

† Under copolymerization, the molar ratio of VP, LMA, TEGDM, and 1-decanethiol (DT) as a chain transfer agent was 80 : 20 : 12 : 12. The distribution of monomer units in the polymer chains was determined by their reactivity. The reactivity of methyl methacrylate (a linear analogue of TEGDM) is much higher than that of VP.[11] The attaching of predominantly active TEGDM fragments by growing polymer radicals of both kinds results in sequential homopolymerization of monomers. Rapidly polymerized methacrylic monomer gives a hydrophobic moiety of the copolymer chain. Afterwards, VP starts to polymerize into the hydrophilic part of the polymer chain.

‡ IR spectra were recorded on a Specord M80 spectrophotometer. ^{1}H NMR spectra of copolymer were recorded on an AVANCE III 500 MHz Bruker BioSpin NMR-spectrometer using deuterated chloroform as a solvent at 295 K. The concentrations of the polymers in chloroform were 3 mg cm^{-3}.

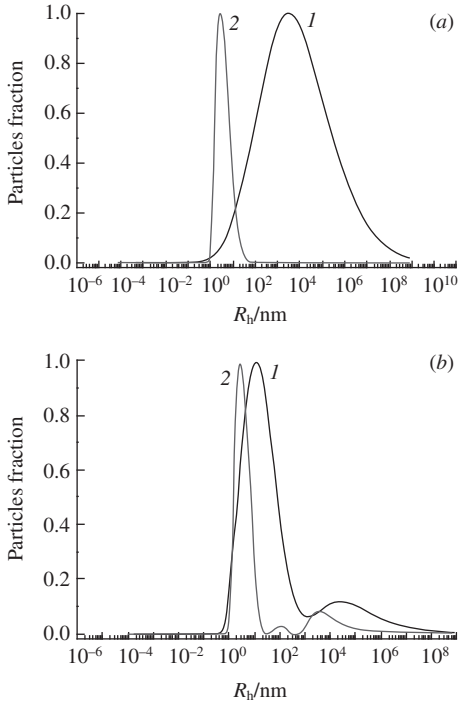


Figure 1 The curves of the particle size distribution (T = 25 °C) in the solutions containing (*1*) 7 and (*2*) 15 mg cm^{-3} of (*a*) copolymer and (*b*) HMMS (*1*) **1** and (*2*) **2** prepared in the respective solutions.

respectively. A notable difference in the measured molecular weights of the copolymer indicated its branched nature.

The second virial coefficient A_2 is above zero for PVP in ethanol[15] or below zero for polybutyl methacrylate in Pr^{i}OH.[16] These suggest Pr^{i}OH to be a 'good' and 'bad' solvent for hydrophilic and hydrophobic fragments of VP–LMA–TEGDM copolymer, respectively. As a result, the amphiphilic macromolecules can form micelle-like aggregates in solution. DLS[§] measurements of copolymer solutions of various concentrations directly confirm the formation of aggregates in a polar solvent. The break point on the dependence of average light scattering intensity I on copolymer concentration C at [C] ~ 7 mg cm^{-3} was interpreted as the critical concentration of aggregation. The size distribution curves of the polymer particles vary considerably [Figure 1(*a*)]. The particle size distribution in a solution containing 15 mg cm^{-3} copolymer becomes narrow and uniform.

The average hydrodynamic radius R_h of the polymer particles does not change substantially with temperature up to 50 °C. Obviously, at [C] > 7 mg cm^{-3} solution contains stable micellar aggregates. At lower concentrations, the solution presents a disordered dispersion. It contains isolated macromolecules and unstable polymeric aggregates of various sizes.

For the HMMS preparation, we used Pr^{i}OH solutions containing either 7 or 15 mg cm^{-3} of the copolymer and fullerene in freshly distilled toluene (0.7 mg cm^{-3}). Special measurements showed the characteristic break point on the dependence of the average scattering intensity I on [C] in Pr^{i}OH – 2.5 vol% toluene mixture owing to stable aggregates in solution. Consequently, a small addition of toluene does not affect the solution structure. The fullerene solution in toluene was added dropwise to a copolymer solution in Pr^{i}OH with continuous agitation by a magnetic stirrer at 22 °C. Conditions of HMMS preparation and C_{60} content per copolymer in solution are given in Table 1.

Table 1 Conditions of HMMS formation in Pr^{i}OH at [C_{60}] = 0.7 mg cm^{-3}.[a]

HMMS	[Copolymer]/ mg cm^{-3}	The volume ratio of the copolymer solution in Pr^{i}OH/C_{60} in toluene	[C_{60}] per copolymer (%)	The precipitate in solution
1	7	4:0.1	0.25	No
2	15	4:0.1	0.12	No
3	7	4:0.3	0.75	Yes
4	15	4:0.3	0.35	Yes

[a] The solubility of C_{60} in toluene[17] at room temperature is ~2.9 mg cm^{-3}. At this C_{60} in toluene is in the form of clusters which are degraded only under very high dilution (at a concentration of three orders of magnitude less than the concentration of a saturated solution). The low concentration of the fullerene in toluene can promote the formation of inclusion complexes where C_{60} is dispersed as molecular form or small clusters.

The HMMS formation was controlled by absorption spectroscopy. Absorption spectra[¶] of the copolymer solution after addition of the fullerene in toluene, and the blank experiment (in the absence of the copolymer) were recorded [Figure S1(*a*), Online Supplementary Materials]. There are the characteristic absorption band of the native fullerene at λ = 330 nm and noticeable absorption in the visible region in the spectra of C_{60} in Pr^{i}OH, indicating the presence of large particles in the solution. The same absorption band of the fullerene is observed in the absorption spectra of HMMS **1** and **2** in solution, and, its optical density is higher than that in a solution without copolymer. No absorption corresponding to fullerene aggregates was detected in the visible region of the spectrum. Under these conditions, the fullerene and/or fullerene-large polymer particles are not precipitated due to aggregation. The whole fullerene was solubilized by copolymers and HMMS **1** and **2** present in solution.

A different mechanism of HMMS formation in copolymer solutions could be assumed. The fullerene enters in the cavity of the polymer coil or adsorbs on it from the solution containing 7 mg cm^{-3} of the copolymer that is mainly a dispersion of individual macromolecules. Meantime, the fullerene aggregates with polymeric micelles in the solution of the polymer colloid adsorbed inside hydrophobic core. In both cases, host–guest inclusion complexes are formed, in which the fullerene is retained by copolymer due to non-bonded interactions.

Over time, a clear HMMS **1** solution takes yellowish, and its absorption spectrum is changed: after two days the absorption band of C_{60} at λ = 330 nm transformed significantly. Its optical density decreased, and absorption at 350–550 nm increased apparently as the result of complex formation between an electron acceptor (the fullerene) and donor groups of the copolymer. The formation of a charge-transfer complex between the fullerene and hydrophilic donor occurs when they reach a distance of at least 4–6 Å.[18] Such linear PVP/ fullerene complex was described previously.[19–23] The fullerene in HMMS **1** is apparently surrounded by polar groups of copolymer; thus, the necessary conditions for donor-acceptor bonding occur. Meanwhile, the HMMS **2** solution did not change its visual characteristics over time, staying to be clear and colorless. The optical density of the fullerene absorption band in the absorption spectrum decreased slightly. In HMMS **2** the fullerene located apparently in the cavities of hydrophobic core of polymer micelles; it hinders the formation of a donor–acceptor complex and retards the fullerene binding with donor groups of the copolymer.

According to DLS, the average scattering intensity of HMMS **1** solution increases twice with respect to initial copolymer solu-

[§] The solutions were preliminarily filtered through a pore diameter of 0.45 μm filter. Prior to measurement, the vials with the solution were thermostated at 20 °C for ~1 h. DLS measurements were carried out on the detection angle 90° using Photocor Compact (Photocor Instruments Inc., USA) equipped with a diode laser operating at a wavelength of 654 nm. The experimental data were processed using the DynaLS v. 2.8.3 software.

[¶] Absorption spectra of the solutions were recorded with a Specord M40 spectrophotometer; the optical path length of the cell was 1 cm.

tion. The narrow peak at low R_h values and a wide one indicating the presence of large aggregates in solution were observed on the size distribution curve of the particles [Figure 1(b), curve *1*]. Particles with R_h of 20–30 nm dominated in solution (~80%); they were insensitive to temperature from 25 to 40 °C. The fullerene deposited on the polymer coil can serve as a core for intermolecular complex formation. The attachment of several polymer coils owing to multiple acceptor centers of the fullerene is probable. Meanwhile, the average scattering intensity of HMMS **2** solution was almost unchanged because of the absence of any aggregation of fullerene–polymer particles. The narrow peak of polymer aggregates remained in the particle size distribution curve [Figure 1(*b*), curve *2*].

We obtained the nanostructures similar to HMMS **1** and **2** at other copolymer concentrations of 3, 5 and 10 mg cm^{-3} below and above the critical concentration point at $I(C)$ curve and the same ratio of the copolymer solution in Pr^{i}OH and the C_{60} in toluene.

To increase the fullerene content per copolymer, we added a 0.3 ml solution of C_{60} in toluene to solutions containing either 7 or 15 mg cm^{-3} of the copolymer. The HMMS **3** and **4** formation was accompanied by the precipitation of the fullerene and large fullerene–copolymers. The precipitate contents of solutions were 17 and 14 wt%, respectively. Dry precipitates were dissolved in 4 ml of chloroform. Intense absorption band of the fullerene at $\lambda = 330$ nm was observed in the absorption spectra of both solutions. According to its optical density, the amount of the fullerene aggregates in Pr^{i}OH is significantly higher for HMMS **4** formation. FTIR data confirm the presence of the copolymer in the analyzed precipitations. According to DLS, the mean light scattering intensity in HMMS **3** solution increased by almost three times compared with the initial copolymer solution, as in the case of the HMMS **1** solution. Meanwhile, the mean intensity of light scattering of HMMS **4** solution was practically unchanged compared with micellar copolymer solution.

Thus, we found the conditions for formation of the HMMS stable in isopropyl alcohol. We obtained hybrid macromolecular nanostructures where the fullerene has been associated with donor groups of the copolymer by donor–acceptor interactions at VP–LMA–TEGDM terpolymer concentrations below or near the critical concentration of aggregation in Pr^{i}OH. The hybrid macromolecular structures in which the fullerene associated with the polymer matrix only by hydrophobic interactions for a long time were formed at copolymer concentrations above the critical concentration of aggregation in Pr^{i}OH. The results of these studies provide new opportunities for the controlled production of polymer inclusion complexes of the fullerene with given physical and chemical parameters and the type of its bonding with the polymer matrix.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.09.011.

References

1 *Developments in Block Copolymer Science and Technology*, ed. I. W. Hamley, John Wiley, New York, 2004.
2 T. Metanawin, T. Tang, R. Chen, D. Vernon and X. Wang, *Nanotechnology*, 2011, **22**, article no. 235604.
3 X. S. Wang, T. Metanawin, X. Yu. Zheng, P. Y. Wang, M. Ali and D. Vernon, *Langmuir*, 2008, **24**, 9230.
4 X. L. Chen and S. A. Jenekhe, *Langmuir*, 1999, **15**, 8007.
5 W. Zhang, R. V. Honeychick and A. Hussam, *Langmuir*, 1996, **12**, 1402.
6 G. Mountrichas, S. Pispas, E. Xenogiannopoulou, P. Aloukos and S. Couris, *J. Phys. Chem. B*, 2007, **111**, 4315.
7 A. Laiho, H. A. Ras Robin, S. Valkama, J. Ruokolainen, R. Osterbaska and O. Ikkala, *Macromolecules*, 2006, **39**, 7648.
8 A. B. Kornev, A. S. Peregudov, V. M. Martynenko, G. V. Guseva, T. E. Sashenkova, A. Yu. Rybkin, I. I. Faingold, D. V. Mishchenko, R. A. Kotelnikova, N. P. Konovalova, J. Balzarini and P. A. Troshin, *Mendeleev Commun.*, 2013, **23**, 323.
9 S. V. Kurmaz, N. A. Obraztsova, E. O. Perepelitsina, D. V. Anokhin, G. V. Shilov, E. N. Kabachkov, V. I. Torbov and N. N. Dremova, *Polym. Composite*, 2014, **35**, 1362.
10 S. V. Kurmaz, N. A. Obraztsova and A.V. Ivanchikhina, *High Energy Chem.*, 2014, **48**, 42 (*Khim. Vys. Energ.*, 2014, **48**, 63).
11 D. F. Grishin, E. V. Kolyakina, V. V. Polyanskova and I. D. Grishin, *Russ. J. Appl. Chem.*, 2007, **80**, 122 (*Zh. Prikl. Khim.*, 2007, **80**, 123).
12 S. V. Kurmaz and A. N. Pyryaev, *Polym. Sci., Ser. B*, 2010, **52**, 1 (*Vysokomol. Soedin., Ser. B*, 2010, **52**, 107).
13 S. V. Kurmaz, G. A. Grubenko, E. I. Knerelman, G. I. Davydova, V. I. Torbov and N. N. Dremova, *Mendeleev Commun*., 2014, **24**, 125.
14 T. P. Klimova, T. A. Babushkina and V. Yu. Khvostova, *Russ. Chem. Bull., Int. Ed*., 2005, **54**, 2452 (*Izv. Akad. Nauk, Ser. Khim*., 2005, 2377).
15 E. Urinov, F. T. Abdullaev and U. M. Mirzaev, *Vysokomol. Soedin., Ser. A*, 1989, **31**, 602 (in Russian).
16 R. Van Leemput and R. Stein, *J. Polym. Sci. A*, 1964, **2**, 4039.
17 V. N. Bezmel'nitsyn, A. V. Eletskii and M. V. Okun', *Physics-Uspekhi*, 1998, **168**, 1091 (*Usp. Fiz. Nauk*, 1998, **168**, 1195).
18 Z. V. Šaponjić, J. M. Nedeljković and M. M. Dimitrijević, *Chem. Phys. Lett.*, 1997, **277**, 335.
19 L. V. Vinogradova, E. Yu. Melenevskaya, A. S. Khachaturov, E. E. Kever, L. S. Litvinova, A. V. Novokreshchenova, M. A. Sushko, S. I. Klenin and V. N. Zgonnik, *Polym. Sci., Ser. A*, 1998, **40**, 1152 (*Vysokomol. Soedin., Ser. A*, 1998, **40**, 1854).
20 V. A. Reznikov, E. Yu. Melenevskaya, L. S. Litvininova and V. N. Zgonnik, *Polym. Sci., Ser. A*, 2000, **42**, 137 (*Vysokomol. Soedin., Ser. A*, 2000, **42**, 229).
21 O. V. Ratnikova, E. Yu. Melenevskaya, M. V. Mokeev and V. N. Zgonnik, *Russ. J. Appl. Chem.*, 2003, **76**, 1620 (*Zh. Prikl. Khim*., 2003, **76**, 1663).
22 E. Yu. Melenevskaya, O. V. Ratnikova, N. P. Yevlampieva, I. I. Zaitseva, V. T. Lebedev, D. N. Orlova, M. N. Mokeev, A. S. Khachaturov and V. N. Zgonnik, *Polym. Sci., Ser. A*, 2003, **45**, 627 (*Vysokomol. Soedin., Ser. A*, 2003, **45**, 1090).
23 I. I. Khairullin, Yu-H. Chen and L.-P. Hwang, *Chem. Phys. Lett*., 1997, **275**, 1.

Received: 4th March 2015; Com. 15/4577