

FABRICATION AND AFM/FFM STUDIES OF C₆₀-CONTAINING POLYELECTROLYTE SELF-ASSEMBLED FILMS*

Lan Huang**, Xiao-rong Hou, Yuan-kang He, Xiao-liang Zheng, Fang Wei,
Xin-sheng Zhao and Wei-xiao Cao

College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Abstract An initial investigation on the roughness and frictional properties of the self-assembled thin films from polyelectrolytes is presented. Star-shaped C₆₀-poly(styrene-maleic anhydride) was successfully prepared. The multilayer thin films have been fabricated on mica with diazoresin as the cationic polyelectrolyte and hydrolyzed star-shaped C₆₀-poly(styrene-maleic anhydride) as the anionic polyelectrolyte via self-assembly technique. The crosslinking structure of the films is formed from the conversion of ionic bond to covalent bond after UV irradiation. AFM/FFM investigations provide insights into the roughness and frictional properties on a microscale. The roughness depends strongly on the number of film layers in the case of C₆₀-containing films. The frictional forces of the films exhibited a well behaved non-linear relationship in response to the change of applied load. It supports the prediction of enhanced load-bearing property of C₆₀-containing thin films.

Keywords Star-shaped C₆₀-poly(styrene-maleic anhydride), Self-assembly film, AFM/FFM, Roughness, Frictional properties

INTRODUCTION

Since Klein's pioneering work^[1], the ordered thin polymer films on solid surfaces have been receiving attention because of their application in microtribology and lubricants since their thickness can be precisely controlled on a molecular scale^[2–5].

The self-assembly technique involving two oppositely charged components has developed rapidly^[6–9], and is used in many fields including microtribology^[10–12]. Recently, the covalently attached multilayer assemblies were reported by Zhang and Cao^[13–20], the thin multilayer films from diazoresin and different negatively charged polyelectrolyte were prepared via the self-assembly technique, and then the crosslinking structure was formed from the conversion of ionic bond to covalent bond after UV irradiation. It has been confirmed that the film stability towards polar solvents can be improved significantly.

The tribological properties of C₆₀ films have been widely studied because of their potential use as solid lubricant, but the experimental observations of the lubricating properties of C₆₀ films were inconsistent^[21–25]. In recent years, the C₆₀-containing polymers were synthesized for lubricating research. It was found that the soft polymer chains attached to C₆₀ can reasonably reduce the friction efficiency, while the C₆₀ cores in the thin film are beneficial for load-bearing capacity^[26–28].

In this paper, the self-assembled thin films fabricated from diazoresin as a positively charged component and hydrolyzed star-shaped C₆₀-styrene-maleic anhydride copolymer as a negatively charged component are reported. The roughness and microtribological properties of these self-assembled films after UV irradiation were investigated primarily by atomic force microscopy/friction force microscopy (AFM/FFM).

* This project is financially supported by the National Natural Science Foundation of China (No. 59843008).

** Corresponding author: Lan Huang (黄兰), E-mail: huangli@pku.edu.cn

Received May 8, 2001; Revised June 11, 2001; Accepted June 12, 2001

EXPERIMENTAL

Materials and Measurements

C₆₀ powder with a purity of more than 99.9% was obtained from Peking University. All the other chemicals were obtained from the Beijing Chemical Factory. Styrene was washed with NaOH solution to remove stabilizer, dried with CaCl₂ overnight, distilled under reduced pressure, and sealed for preservation at low temperature. Benzoyl peroxide (BPO) was recrystallized by chloroform. 1,2-Dichlorobenzene was distilled under reduced pressure. Other chemicals and solvents were used as received.

The M_w of the polymer was measured by using a Waters GPC instrument with a 515 pump, a 2410 refractive index detector, a 2487 dual λ absorbance detector and three Styragel columns HT2 + HT3 + HT4 connected in series. Polystyrene standards with dispersity of 1.08–1.12 and THF as eluent at 1 mL/min flow rate were used. UV spectra were recorded using a Shimadzu 2100 UV-Vis spectrophotometer. The experiments on roughness and friction property were performed by atomic force microscope/friction force microscope (AFM/FFM) with Digital Nanoscope IIIa, Si₃N₄ tip, $K = 0.06$ N/m cantilever, tipping mode and contact mode.

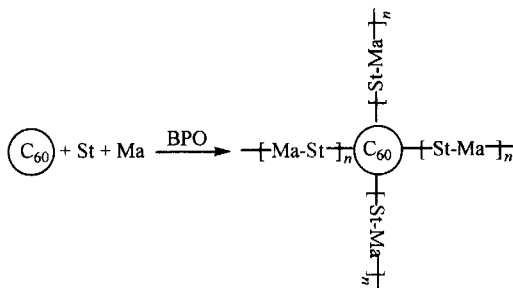
Synthesis of Star-shaped C₆₀-Styrene-Maleic Anhydride Copolymer [C₆₀-poly (St-Ma)]

Based on Guan's work^[27], star-shaped C₆₀-styrene-maleic anhydride copolymer with different M_w and C₆₀ contents were prepared by solution polymerization using BPO as the radical initiator and 1,2-chlorobenzene as the solvent.

In a typical polymerization, 50 mg C₆₀ was dissolved in 20 mL 1,2-chlorobenzene to get the purple solution. 100 mg BPO, 500 mg maleic anhydride and 500 mg styrene were added to the solution under stirring. After they have been deoxygenated by bubbling dry nitrogen gas for 10 min, the solution was heated to ~75 °C and kept for 24 h under N₂. The blank sample (styrene-maleic anhydride copolymer) was prepared under the same conditions.

The copolymers formed in the reaction were precipitated out by adding 150 mL methanol and filtered off. The brown crude product was dissolved in 20 mL THF and precipitated by adding 100 mL methanol, filtered off, washed with methanol, dried in a vacuum oven. A light brown powder product (0.83 g) was obtained. The products can be dissolved in some organic solvents, such as chloroform and tetrahydrofuran.

The valuable insight of the multiple radical addition of C₆₀ came from the ESR spectroscopy and ¹³C-NMR investigation^[28]. The star-shaped C₆₀-styrene copolymers were first prepared by Cao and Webber^[29] by free radical copolymerization. It was shown that the copolymerization can be accomplished by the use of a radical initiator and the copolymers of C₆₀-styrene are random copolymers. These authors concluded that the propagation of C₆₀ radicals is slow in general because of their relatively high stability^[30]. It has been suggested^[31] that C₆₀ competes effectively with styrene for the initiator radicals and PS radicals as well; *i.e.* namely, C₆₀ may act as a radical inhibitor in the copolymerization reactions.



Scheme 1

In the copolymerization of C₆₀-styrene-maleic anhydride, the contribution of poly(styrene-maleic anhydride) alternate structure is still substantial because of its large population. The formation of star-shaped C₆₀-styrene-maleic anhydride copolymer [C₆₀-poly(St-Ma)] is illustrated in Scheme 1.

The typical copolymerization conditions of C₆₀-poly(St-Ma) and the GPC analysis are listed in Table 1.

Table 1. The results of copolymerization of C₆₀-styrene-maleic anhydride

Sample no.	C ₆₀ (mg)	BPO (mg)	St (mg)	Ma (mg)	M_n	M_w	Dispersity
H1123	0	100	500	500	6085	8580	1.41
H1116	25	100	500	500	6497	8623	1.32
H1222	40	100	500	500	5151	8448	1.64
H0105	50	100	500	500	4992	8786	1.76
H0108	60	100	500	500	4316	8545	1.98
H0225	75	100	500	500	2553	5923	2.32

As we can see from Table 1, the more C₆₀ content in the feed, the lower is the molecular weight and higher is the dispersity of the product.

As usual, the refractive index detector in the GPC instrument was used to detect the products in the eluent. Since C₆₀ has a characteristic absorption at $\lambda = 350$ nm while the blank sample does not^[32], the UV detector used to determine the presence of C₆₀ in the products. Figure 1 shows the presence of C₆₀ which is chemically bonded with poly(styrene-maleic anhydride) chains in the products.

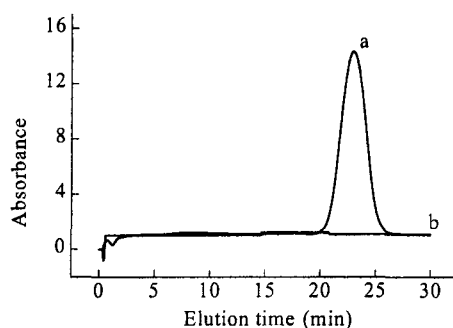


Fig. 1 The GPC diagrams of star-shaped C₆₀-poly(St-Ma) (a) and poly(St-Ma) (b) using UV detector at $\lambda = 350$ nm

Fabrication of Films from Diazoresin and Hydrolyzed C₆₀-poly(St-Ma)

Diazoresin (DAR) was prepared according to the method described elsewhere^[33], its $M_n \approx 2500$ g/mol.

The hydrolyzed C₆₀-poly(St-Ma) was prepared via the hydrolysis of the parent copolymer in 5% NaOH aqueous solution under refluxing. The hydrolysate was filtered and precipitated with ethanol and dried in vacuum at 60 °C.

The fabrication of films was conducted in the dark at room temperature. Freshly cleaved mica, which has a negatively charged surface in water was used as the substrate. The mica was first immersed in DAR aqueous solution (2 mg/mL) for 5 min, after rinsing with deionized water and air drying, the mica was immersed in the hydrolyzed C₆₀-poly (St-Ma) aqueous solution (2 mg/mL) for 5 min before rinsing and drying as above. On repeating the procedures, a layer-by-layer self-assembled polyelectrolyte film was obtained. In this paper, films with 1 bilayer, 6 bilayers and 12 bilayers were prepared.

The films were irradiated with a 80 W medium pressure mercury lamp at a distance of 13 cm for 30 s.

AFM/FFM

The measurements were performed with a Nanoscopy IIIa (Digital Instruments, Inc.) equipped with a bioscope G scanner (90 μ m) in contact mode and tapping mode, respectively. A commercial Si₃N₄ cantilever with a spring constant of $K = 0.06$ N $\cdot$ m⁻¹ was used. The images were obtained in air at 25 °C and relative humidity 50% with 2 Hz scan rates.

Roughness images and root mean square (RMS) were obtained simultaneously when the scan angle was 0°. Friction images in trace and retrace scan directions were recorded when the scan angle was 90°, with different applied load, the friction forces (V) were then plotted as a function of load to yield a friction-load map^[34].

RESULTS AND DISCUSSION

Structure of Self-assembled Film

The fabrication was monitored by measuring the UV absorbance of the films at $\lambda = 383$ nm, which is the characteristic absorption of the diazonium group of DAR. In Fig. 2, the absorbance at 383 nm increases with the increasing of number of bilayers.

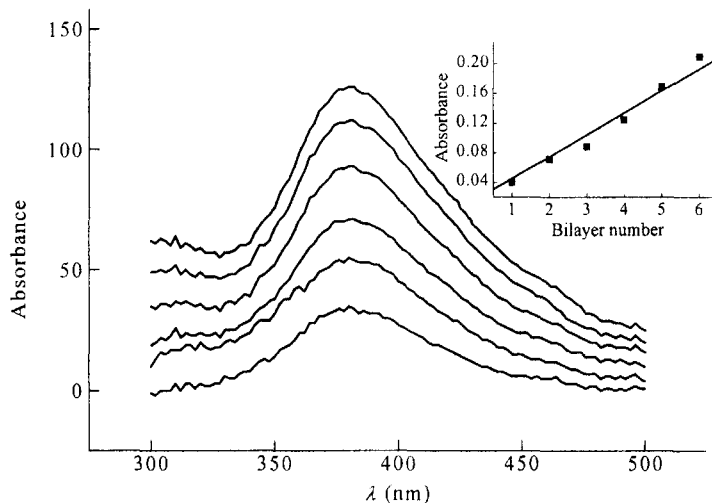
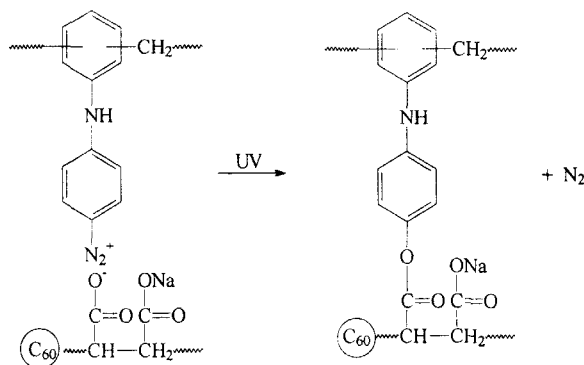


Fig. 2 Absorbance of the multilayer film at 383 nm with different numbers of bilayers
Bilayer numbers (from bottom to top): 1, 2, 3, 4, 5, 6

This constitutes convincing evidence that the films are formed via layer-by-layer self-assembly.

After the photoreaction, the diazonium groups were decomposed and the crosslinking structure of the multilayer film was formed via the conversion of ionic bonds to covalent bonds, mainly ester bonds, as shown in Scheme 2. This was confirmed by FTIR studies elsewhere^[35].



Scheme 2 The bond conversion taken place in hydrolyzed star-shaped C_{60} -poly(St-Ma)/DAR multilayer film under UV irradiation

The films consisting of both cationic and anionic groups exhibit an extremely high tendency to aggregate by the ionic attractive force. The conversion of ionic bonds into covalent bonds makes the multilayer self-assembled films more stably packed. This is schematically represented in Fig. 3.

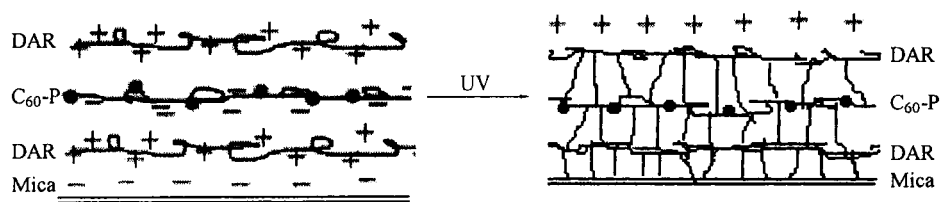


Fig. 3 Schematic diagram of the structural changes of multilayer films of hydrolyzed star-shaped C₆₀-poly(St-Ma)/DAR after UV irradiation

Roughness Images

Figure 4 shows the representative AFM images of the C₆₀-containing self-assembly films with different number of bilayers after UV irradiation.

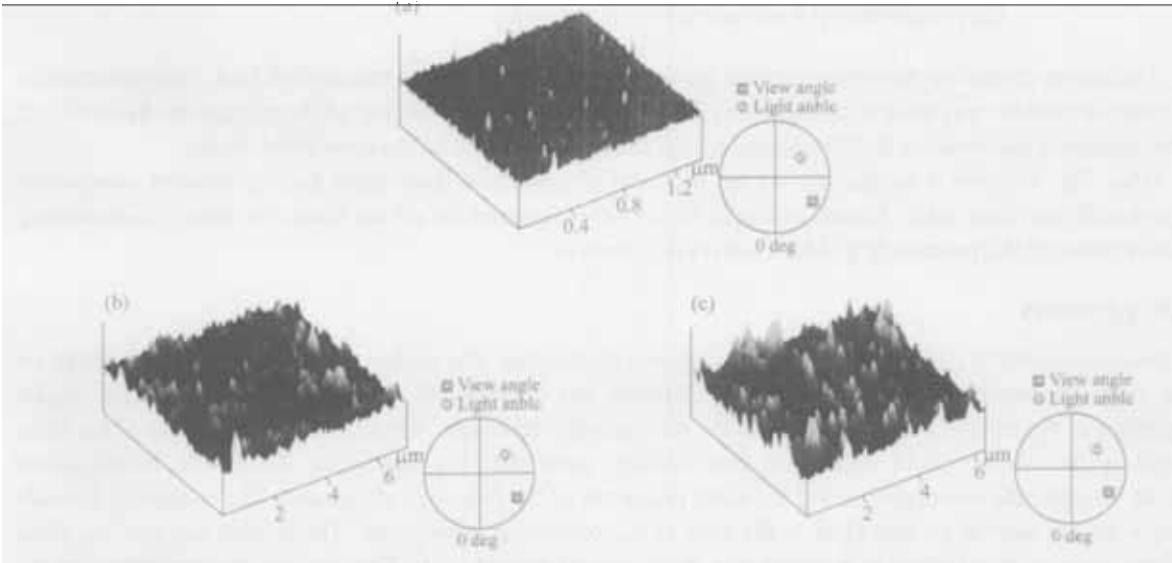


Fig. 4 Tapping mode AFM images of 1 bilayer (a), 6 bilayers (b) and 12 bilayers (c) of hydrolyzed star-shaped C₆₀-poly(St-Ma)/DAR self-assembly film ($M_n = 5100$)

Enhanced brightness in the images corresponds to increased height in the Z-direction. The data of RMS are listed as follows:

Bilayer	1	6	12
RMS(nm)	0.895	5.780	12.256

It is observable that 1 bilayer film is rather flat and uniform compared to the others. The RMS varies with the number of bilayer of films, and increases the defects in the process of self-assembly from C₆₀-containing polyelectrolyte. We presume that the intrinsic molecular chains were locally disordered in the C₆₀-containing copolymers, and the existence of interpenetrating structures between the layers^[19].

Frictional Properties

A typical approach to characterize the friction properties of thin films is to investigate the relation between the friction force and the applied load in the trace-retrace friction image. The friction force can be measured at different applied load at the same area in the FFM map.

Figure 5 shows the overlap of four different friction force versus load curves obtained from 1 bilayer, 6 bilayers, 12 bilayers of C_{60} -containing self-assembly films and the fresh clean mica surface, respectively.

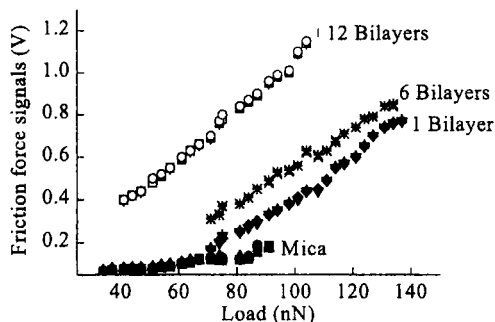


Fig. 5 Diagrams of frictional force signal versus load for hydrolyzed star-shaped C_{60} -poly(St-Ma)/DAR self-assembly films and mica

The curves reveal the non-linear relation between the friction force and the applied load. Film deformation and material transfer was not evidenced during FFM measurement. The stability of these films can be attributed to the additional load-bearing ability afforded by C_{60} chemically bonded on the copolymer chains.

Also, Fig. 5 shows a comparison of the frictional properties of these films having different numbers of bilayers with the clean mica. Higher frictional forces were observed for all the films, yet these C_{60} -containing polymer films exhibit reasonably good frictional performances.

CONCLUSIONS

We have succeeded in synthesizing C_{60} -containing polyelectrolytes. The multilayer thin films were fabricated on mica with diazoresin as the cationic polyelectrolyte and hydrolyzed star-shaped C_{60} -poly(styrene-maleic anhydride) as the anionic polyelectrolyte via the self-assembly technique. The crosslinking structure of the films formed by the conversion of ionic bond into covalent bond after UV irradiation. AFM/FFM investigations provide insights into the roughness and frictional properties of the films on a microscale. The roughness depends strongly on the number of film layer in the case of C_{60} -containing copolymers. The friction force of the films exhibits a non-linear relationship in response to the change of applied loads. This supports the prediction that the load-bearing property of C_{60} -containing copolymer thin films is enhanced.

REFERENCES

- 1 Klein, J., Kumacheva, E., Mahalu, D., Perahia, D. and Fetters, L.J., *Nature*, 1994, 370: 634
- 2 Bhushan, B., Israelachvili, J.N. and Landman, U., *Nature*, 1995, 374: 607
- 3 Zhang, Z.J., Xue, Q.J. and Zhang, J., *Wear*, 1997, 209: 8
- 4 Maboudian, R. and Howe, R.T., *J. Vac. Sci. Technol. B*, 1997, 15: 1
- 5 Shon, Y.S., Lee, S., Colorado, R., Perry, S.S. and Lee, T.R., *J. Am. Chem. Soc.*, 2000, 122: 7556
- 6 Decher, G., Hong, J.D. and Schmidt, J., *Thin Solid Film*, 1992, 210: 831
- 7 Decher, G., *Science*, 1997, 277: 1232
- 8 Losche, M., Schmitt, J., Decher, G., Bouuman, W.G. and Kristain, K., *Macromolecules*, 1998, 31: 8893
- 9 Tarabia, M., Hong H., Davidov, D., Kirstein, S., Neumann, R. and Avny, V., *J. Appl. Phys.*, 1998, 83: 725
- 10 Chen, J.Y., Huang, L., Ying, L.M., Luo, G.B., Zhao, X.S. and Cao, W.X., *Langmuir*, 1999, 15: 7208
- 11 Lee, S., Shon, Y.S., Lee, T.R. and Perry, S.S., *Thin Solid Films*, 2000, 358: 152
- 12 Huang, L., Luo, G.B., Zhao, X.S., Chen, J.Y. and Cao, W.X., *J. Appl. Polym. Sci.*, 2000, 78: 631
- 13 Sun, J.Q., Wu, T., Sun, Y.P., Wang, Z.Q., Zhang, X., Shen, J.C. and Cao, W.X., *Chem. Commun.*, 1998, 1853

- 14 Sun, J.Q., Wang, Z.Q., Zhang, X., Shen, J.C. and Cao, W.X., *Chem. Commun.*, 1999, 693
- 15 Zhang, X. and Shen, J.Q., *Advanced Materials*, 1999, 11: 1139
- 16 Chen, J.Y. and Cao, W.X., *Chem. Commun.*, 1999, 1703
- 17 Chen, J.Y., Luo, H. and Cao, W.X., *Polym. Int.*, 2000, 49: 382
- 18 Sun, J. Q., Wu, T., Liu, F., Wang, Z.Q., Zhang, X. and Shen, J.C., *Langmuir*, 2000, 16: 4620
- 19 Sun, J.Q., Cheng, L., Liu, F., Dong, S.J., Wang, Z.Q., Zhang, X. and Shen, J.C., *Colloids and Surface A*, 2000, 169: 209
- 20 Wang, R.X., Chen, J.Y. and Cao, W.X., *J. Appl. Polym. Sci.*, 1999, 74: 189
- 21 Schwarz, U.D., Allers, W., Gensterblum, G. and Wiesendanger, R., *Phys. Rev. B*, 1995, 52: 14976
- 22 Luengo, G., Camphell, S.E., Srdanov, V.I., Wudi, F. and Israelachvili, J.N., *Chem. Mater.*, 1997, 9: 1166
- 23 Nakagawa, H., kibi, S., Tagawa, M., Umeno, M. and Ohmae, N., *Wear*, 2000, 238: 45
- 24 Schwarz, U.D., Zworner, O., Kister, P. and Wiesendanger, R., *Phys. Rev. B*, 1997, 56: 6987
- 25 Tsukruk, V. V., Everson, M. P., Lander, L. M. and Brittain, W. J., *Langmuir*, 1996, 12: 3905
- 26 Shi, B., Huang, L., Wang, J.H., Qian, L.M., Luo, J.B. and Hong, H., *Chinese J. Mater. Res.*, 1997, 11: 346
- 27 Guan, W.C., Lei, H. and Liao, D.X., *Chem. J. of Chinese Univ.*, 2000, 21: 1149
- 28 Krusic, P.J., Wasserman, E., Keizer, P.N., Morton, J.M. and Preston, J.F., *Science*, 1991, 254: 1183
- 29 Cao, T. and Webber, S.E., *Macromolecules*, 1995, 28: 374
- 30 Morton, J.M., Preston, J.F., Krusic, P.J., Hill, S.A. and Wasserman, E., *J. Phys. Chem.*, 1992, 96: 3576
- 31 Cao, T. and Webber, S.E., *Macromolecules*, 1996, 29: 3826
- 32 Zhou, P., Chen, G.Q., Hong, H., Du, F.S., Li, Z.C. and Li, F.M., *Macromolecules*, 2000, 33: 1948
- 33 Cao, S., Zhao, C. and Cao, W., *Polym. Int.*, 1998, 45: 142
- 34 Li, J.W., Wang, C., Shang, G.Y., Xu, Q.M., Lin, Z., Guan, J.J. and Bai, C.L., *Langmuir*, 1999, 15: 7662
- 35 Luo, H., Chen, J.Y., Luo, G.B., Chen, Y.N. and Cao, W.X., *J. Mater. Chem.*, 2001, 11: 419