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Self-assembly of segmented polyurethane and poly(4-vinylpyridine) in solution

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Summary

Poly(tetrahydrofuran) (PTHF) reacted with toluene diisocyanate (TDI) to form a prepolymer. Such a prepolymer was extended by 2,2-hydroxymethyl butanoic acid (DMBA) to form a segmented polyurethane with carboxyl (PUc) consisting of alternating soft and hard segments, where carboxyls are distributed only along the hard segments. By using static and dynamic laser light scattering (LLS) as well as atomic force microscopy (AFM), we have investigated the self-assembly of the PUc and poly(4-vinylpyridine) (P4VP) in tetrahydrofuran/chloroform mixed solvent. Our experiments show that the PUc and P4VP form a stable assembly with a size of 59-122 nm due to the H-bonding, depending upon the PUc (COOH) concentration. The LLS and AFM measurements demonstrate the assembly is spherical.

Introduction

Self-assembly of polymers has been one of the most prevalent research subjects in polymer science during the past decades [1-2]. Polymer micelles with nano-structure are especially of interest because of their potential applications in solubilizers and drug carriers [3-5]. Before the year of 2000, most studies on self-assembly of macromolecules were focused on the micellization of block and graft copolymers in selective solvents [6-8], in which the driving force for the micellization is generally attributed to the differences in solubility between the component blocks. Recently, Jiang et al developed a new approach for self-assembly [9-21]; namely, one polymer (polymer A) is with a H-bond donor while another (polymer B) is with a H-bond acceptor. These two polymers respectively with H-bond donor and acceptor may self-assemble into a micelle-like structure in a solvent mixture, in which one is a precipitant for polymer A but good solvent for polymer B. The compact core of polymer A is stabilized by soluble B chains surrounding the core. Since there are no covalent bonds but specific interactions, such a self-assembly is named as non-covalently connected micelles (NCCM) [22].

The proton-donating polymers employed in the micelle formation through H-bonding are usually the end-functionalized oligomers with different end groups, such as $-CH_2OH$, $-COOH$ and $-N(CH_3)_2$. Among them the end-functionalized polymers with COOH are the most commonly used, including carboxyl-terminated polystyrene (CPS) [16-19], carboxyl-terminated polybutadiene [9], carboxyl-terminated polyimide

[12]. In addition, Jiang et al also studied the self-assembly of homopolymers and random copolymers where the carboxyls are distributed along the backbone [10,11]. Generally, pyridyl and carboxyls act as the H-acceptor and H-donor, respectively.

Polyurethane with carboxyl (PUc) is the segmented copolymer consisting of alternating soft and hard segments. The soft segment is usually a polyether or polyester with molecular weight of 1000-3000, whereas a hard segment contains carboxyls. Since the soft and hard segments are alternatively distributed along polyurethane chain, the carboxyls are blockily distributed.

The multiple H-bonds in PUc itself based on two H-bond donors have been preliminarily studied both by FTIR and molecular mechanics (MM) simulation methods [23-24]. The results show that the main H-bond types are those from both the typical urethane themselves [25-27] and carboxylic dimer. In the present work, a PUc based on poly(tetrahydrofuran) (PTHF), 2,2-hydroxymethyl butanoic acid (DMBA) and toluene diisocyanate (TDI) was prepared. By using static and dynamic laser light scattering (LLS) as well as AFM, we have investigated the assembly formed by PUc and P4VP. The present work is to understand how a segmented polymer assembles with another polymer.

Experimental Section

Materials

TDI (2,4-TDI and 2,6-TDI = 80/20) and PTHF (Mn = 1000 g/mol) were both obtained from German Bayer Co. DMBA was from Japan Nippon Kasei Chemical Co., Ltd. Chloroform and THF were reagents from Shanghai, China. P4VP (Mn = 6×10^4 g/mol) was from Aldrich Chemical Company Inc., which was used as received.

Polymerization

Segmented PUc based on PTHF, TDI and DMBA was synthesized by a two-step procedure in a three-necked flask equipped with a reflux condenser. Prepolymer was firstly synthesized by adding two moles of TDI into one mole of PTHF under N_2 and reacted at 80°C for one hr, then DMBA were stoichiometrically added into the prepared prepolymer to form the multi-segment PUc in acetone. About 50% of the total used acetone was added to the reactant mixture at beginning, heated to its refluxing temperature of acetone under stirring for two hours. The rest acetone was then gradually added during the preparation to keep the reaction going smoothly until the final PUc concentration was about 20%. The acetone in PUc was eventually removed before use. Fig. 1 shows the preparation of PUc.

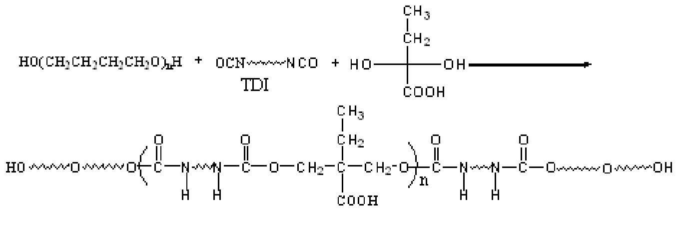

Fig. 1 Preparation of segmented PUc

Instruments

FTIR spectra were recorded on a Shimadzu FTIR-8700 spectrometer from 4000 to 400 cm^{-1} averaging 45 scans at a resolution of 2 cm^{-1}. The PUc solution samples were directly coated onto a piece of KBr plate and measured after the acetone was completely removed.

NMR spectra were available using Bruker 300 ultraNMR spectrometer. The diameter of the tube is 5mm with TMS as internal standard at 25°C. The working frequency used for ^{1}H is 300MHz while that used for ^{13}C is 75 MHz. DMSO-d_6 is used for solvent.

GPC SHIMADZULC-10A type of gel permeation chromatography (GPC) was used to characterize the molecular weight and molecular weight distribution at 25°C. The detector is RIG-10A with polystyrene as standard sample. The solvent used is THF with flowing rate of 1.0 cm^3 min^{-1}. The sample amount is 50μl.

Characterization

FTIR Obvious νN-H at 3300 cm^{-1}, amide II at 1538 cm^{-1} and amide III at 1225 cm^{-1} bands were found in FTIR spectrum in PUc, indicating that urethane group was formed. Meanwhile there is wide νC=O band in 1680-1750 cm^{-1}, showing the existence of different C=O groups from both urethane and carboxyl. In addition, the small band at 2606 cm^{-1} also suggests the existence of COOH. Moreover, νC-O band at about 1100 cm^{-1} shows C-O-C group from soft segment.

^{1}H NMR (DMSO-d_6, TMS): δ12.76 (H from COOH), δ9.50 and δ 8.86 (–NHCOO–), δ7.47 and δ 7.06 (–ph–), δ 4.25 and δ3.402 (–CH_2O–, both from urethane and PTHF), δ 2.10 (CH_3–ph), δ 1.59 (–CH_2– attached to CH_3 in DMBA), δ 0.86 (CH_3 in DMBA).

^{13}C NMR (DMSO-d_6, TMS): *δ*174.78 (–COOH), *δ*153.51 (–NHCOO–); *δ*137.18, *δ*130.16, *δ*115.05 (–ph–), *δ*69.68 and *δ*63.86 (–CH_2O–, both from urethane and PTHF).

GPC Mn is about 5400, Mw is 13000, Mw/Mn is about 2.4.

Above results show that the sample prepared is supposed to be the expected PUc with the structure of soft and hard segments (Fig. 1). Though DMBA has a tertiary carboxyl group, the two primary hydroxyls will react with only isocyanate under normal conditions to form the PUc hard segment. The pendent carboxyl will be only in the hard segment.

Preparation of PUc /P4VP assembly

PUc was dissolved into THF, and P4VP was dissolved into $CHCI_3$, respectively, with the concentration between 10^{-3} to 10^{-4}g/ml. Then addition of P4VP/$CHCI_3$ solution into PUc/THF solution to some extent led to an obvious bluish solution, indicating the occurrence of the assembly. The assembly with different PUc/P4VP composition, and the P4VP in the same mixed solution as a control sample, were also prepared in this way. In preparing P4VP control sample, about 2g P4VP/$CHCl_3$ solution was dropwise added to 11g THF while about 1.6g P4VP/$CHCl_3$ solution was added to 13g PUc/THF solution in preparing PUc/P4VP assembly.

Measurements

LLS A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlation (ALV-5000e) and a He-Ne laser (Uniphase, output power) 22 mW at $\lambda_0 = 632.8$ nm) as light source was used. All measurements were conducted at 25.0 ± 0.01°C. The solutions were clarified using a 0.45 or1.0μm microfilter (Alltech Associates Inc). The specific gravity of $CHCl_3$ is 1.478 g/ml with reflection index of 1.483 and the viscosity parameter of 0.542; the specific gravity of THF is 0.888 g/ml with reflection index of 1.409 and the viscosity parameter of 0.458. The reflection index and viscosity parameter in the mixed solvents were obtained by addition of the relative number values, that is, their own reflection index or viscosity parameter times the actual amount.

From static LLS, the average radius of gyration (R_g) can be available through the following equation:

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_W}[1+\frac{1}{3}q^2 < R^2{}_g >] + 2A_2C$$

Here, $K = 4\pi^2n^2(dn/dC)^2/(N_A\lambda_0^4)$, $q = (4\pi n/\lambda_0)\sin(\theta/2)$, N_A, dn/dC, n, λ_0 are the Avogadros constant, refractive index ratio, solvent refractive index and the light wavenumber in vacuum, respectively.

The average hydrodynamic radius (R_h), on the other hand, can be obtained from dynamic LLS via the Stokes-Einstein equation: $R_h = k_B T / (6\pi\eta D)$. Here k_B, T and η are the Boltzman constant, absolute temperature and the solvent viscosity, respectively.

AFM Tapping mode AFM images were obtained at ambient conditions using a NanoScope III MultiMode AFM (Digital Instruments). Both height and phase images were recorded simultaneously using the retrace signal. Si tips with a resonance frequency of approximately 300 kHz and a spring constant of about 40 N m-1 were used, and the scan rate was in the range 0.5-1.2 Hz.

Results and discussion

LLS results show no obvious aggregate in PUc itself in $CHCl_3$ or THF at very dilute concentration of about 10^{-4}g/ml. Though PUc would be shown some aggregates when its concentration increases to about 10^{-3}g/ml, the size of such aggregate would decrease greatly when the concentration is diluted. It is found that the self-assembly between PUc and P4VP is fundamentally different from PUc itself under the same condition according to the LLS results, as the light scattering intensity from PUc/P4VP assembly is much stronger than that from PUc itself in THF/$CHCl_3$ mixed solution. In addition, the PUc/P4VP assembly is very stable and shows obvious bluish opalescence. P4VP itself, on the other hand, has the same result (about 10 nm and can be taken as no aggregation either) in $CHCl_3$ as ref [19-20] reported. Since PUc and P4VP assembly was eventually realized in THF/$CHCl_3$ mixed solvents, and since it was found that there also appeared obvious bluish opalescence for P4VP itself under the same mixed solvents, we in the present paper mainly study the self-assembly of PUc/P4VP and P4VP control in the same mixed solvents.

Aggregation of P4VP itself in the mixed solvents

Fig. 2 is the R_h distribution of P4VP in $CHCI_3$ at 15° scattering angle, which shows the size is 8-13 nm with the average size of 10 nm, suggesting P4VP does not aggregate in $CHCI_3$. It was found, however, that the similar bluish opalescence like that in PUc/P4VP also appeared when P4VP/$CHCI_3$ solution was dropwise added to THF. Obviously, some aggregation happened, which does not precipitate in the mixed solvents, although P4VP cannot be dissolved in THF. If only judging from the opalescence appearance, it is hard to tell the difference between the aggregation of P4VP itself and the self-assembly of P4VP/PUc.

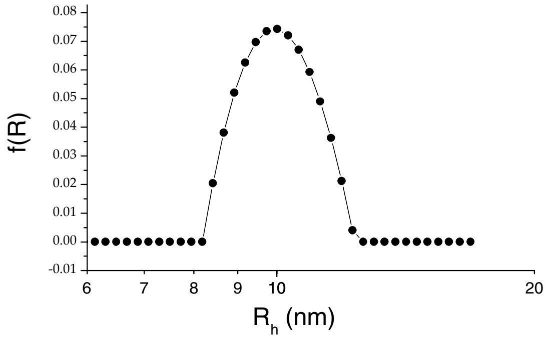

Fig. 2 Hydrodynamic radius (R_h) distributions of P4VP in $CHCI_3$ (Concentration is 1.056×10^{-3}g/ml)

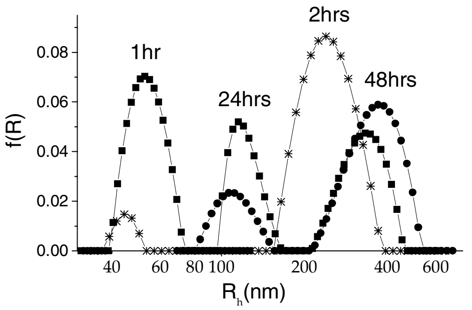

Fig. 3 Hydrodynamic radius (R_h) distributions of P4VP in THF and $CHCl_3$ at different time periods
(Concentration of P4VP/$CHCl_3$ is 1.056×10^{-3}g/ml)

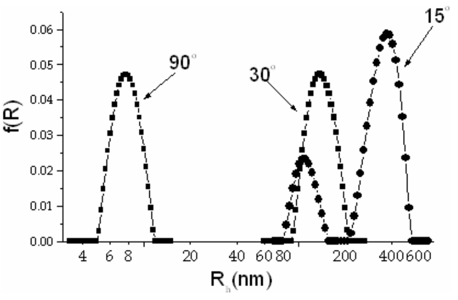

Fig. 4 Hydrodynamic radius distributions of P4VP in THF and $CHCI_3$ at different scattering angles
(Concentration of P4VP/$CHCl_3$ is $1.056\times10^{-}$g/ml)

It can also be found from Fig. 3 and 4, however, that the aggregation (if we call it in this way to express what we observed from LLS result) of P4VP in the mixed solution is unstable. The size would increase with time obviously, and the size distribution is also changeable. In addition, the dependence of scattering angle on the size distribution is also obvious. The size of the aggregate at 90° is only several nanometers, much smaller than that at 15°, suggesting it is not spherical. This result does prove from another respect the indispensable function of the strong H-bond between the two polymers in order to form a stable assembly. Such a strong H-bond may also change and further stabilize the shape of the self-assembly.

Self-assembly of PUc and P4VP

The usual way of making a self-assembly through H-bonding is to put both P4VP and a carboxylated polymer into a common solvent [14-15,17], which is usually $CHCI_3$, then a non-solvent, usually methanol [17], hexane [14] and toluene [15] was added into the solution. We firstly selected $CHCI_3$ as the common solvent for both P4VP and PUc. $CHCI_3$ can be used as solvent for dilute PUc and also for P4VP solution. But the precipitant would immediately appear when P4VP/$CHCI_3$ solution was added into PUc/$CHCI_3$ solution or vice versa, suggesting the self-assembly was formed due to new interaction between PUc and P4VP, but $CHCI_3$ is not its good solvent.

It is found, however, that THF can dissolve the precipitant, indicating THF is good solvent for PUc/P4VP assembly. Then we began using THF as the solvent for PUc. Since THF is non-solvent of P4VP, $CHCI_3$ was still used for dissolving P4VP. Then addition of P4VP/$CHCI_3$ solution into PUc/THF solution to some extent led to an obvious bluish opalescence that indicated the forming of nano- or micro-sized particles. Obviously the core in the assembly is P4VP, as THF can dissolve the assembly but THF is non-solvent of P4VP. Addition of THF into the mixture makes P4VP turn to precipitate. Fig. 5 is the LLS result of R_h distributions of such an assembly, which shows that the peak size is just about 100 nm at the concentration of about 0.001g/ml.

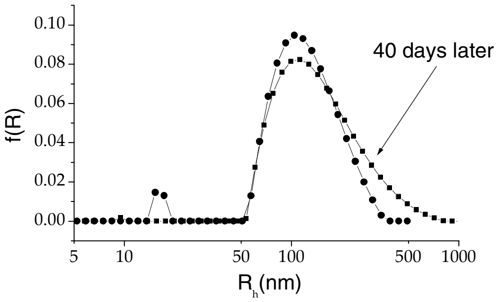

Fig. 5 Comparative hydrodynamic radius (R_h) distributions of PUc/P4VP assembly in mixed solvents (THF+$CHCl_3$) at different time periods (Total concentration is 9.64×10^{-4}g/ml)

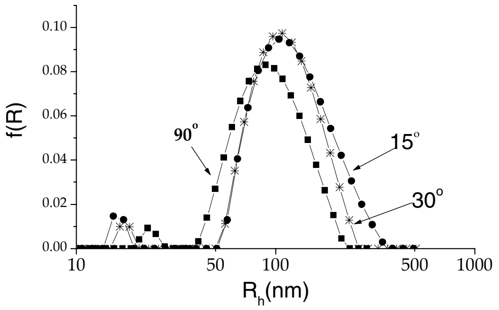

Fig. 6 **Hydrodynamic** radius (R_h) distributions of PUc/P4VP assembly at different angles in THF/$CHCl_3$ mixed solvents (Total concentration is 9.64×10^{-4}g/ml)

It is found that the size of self-assembly is not dependent upon the dilution, even if the solution was diluted for 10 times. In addition, it can be seen from Fig 5 that the size basically remains unchanged with time either. Although the larger size fraction is a bit larger than that of 40 days ago and the smaller size almost disappeared, the peak size and the distribution keep almost the same as 40 days ago. These results suggest that the self-assembly between P4VP and PUc is not only available but very stable as well. In addition, the initial assembly would make some further rearrangement to reach the final balance, as the smaller size of aggregation becomes larger. This can be seen from both the disappearance of 20nm of small aggregation and the widening of the larger size part in Fig. 5. Besides, Fig.6 shows that the size and size distribution are very similar in different scattering angles, suggesting the assembly shape is spherical.

Characteristic of PUc/P4VP Assembly

In order to further investigate the PUc/P4VP assembly, we observed the effect of the PUc concentration on the assembly. Table 1 shows the effect of different PUc concentrations on the R_h, R_g in the assembly when the THF/$CHCl_3$ mixture ratio and P4VP content were fixed. The result shows that the relation between R_g or R_h and PUc concentration is similar. Generally, R_g and R_h increase with PUc concentration. However, the R_g/R_h ratio basically remains unchanged with PUc concentration by keeping 0.8~0.9, suggesting the assembly of PUc/P4VP is spherical. The average assembly size is around 100nm when concentration of PUc/P4VP in $CHCI_3$/THF mixed solvents is about 0.001g/ml (Table 1). It can also be known from Fig. 6 that the size of the self-assembly basically remains unchanged with scattering angles. The spherical self-assembly of PUc/P4VP was also confirmed by AMF. We can observe many small spherical particles from AMF photo (Fig. 7), which also shows the size is just near 100 nm. In addition, it can be seen from Table 1 that the stable assembly can be available in different PUc/P4VP concentrations.

Table 1 LLS results at different PUc concentrations with fixed THF/$CHCl_3$ ratio and P4VP content

Concentration e^{-4}(g/ml)	Weight of PUc in solution (mg)	R_h	R_g	$\langle R_g\rangle/\langle R_h\rangle$
1.26	0.179	58.9	48.5	0.823
3.02	2.714	64.2	54.4	0.847
5.48	6.246	77.7	70.5	0.907
9.64	12.237	100.7	86.9	0.863
19.11	25.882	92.1	79.2	0.860
36.69	51.200	121.3	103.8	0.856

It is worth noting that the instability of either PUc or P4VP in solution just prove again that the H-bonds between PUc and P4VP play the key role in leading to the self-assembly. It is also worth noting that each pyridine unit provides one proton acceptor, whereas each hard segment in PUc may offer two types of H-bond donors, i.e. the H from pendent COOH group and H from urethane group. Therefore, there may have more sites in PUc to form the H-bonds with P4VP. Is it true for the two types of donors to form the H-bond with P4VP in PUc/P4VP assembly? What is the ratio of contribution for the two types of H-bonds to the assembly if it is true? Is there any

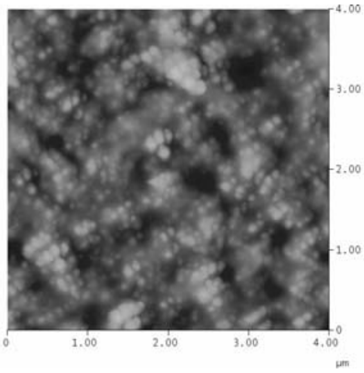

Fig. 7 AFM photo of PUc/P4VP self-assembly in mixed solvents at total concentration of 9.64×10^{-4}g/ml

other H-bonding interaction besides these? Anyway, it can be expected that the H-bond interactions in PUc/P4VP are much more complicated than other self-assembly systems. Some issues still need to be further investigated. We will present our research on these issues in next paper.

Conclusion

Self-assembly of segmented polyurethane with carboxyl (PUc) and poly(4-vinylpyridine) (P4VP) has been successfully prepared in the selected mixed solvents for the first time. The average size of assembly is around 100 nm when PUc/P4VP concentration is about 0.001g/ml. The assembly is stable with time and concentration. The R_g/R_h basically remains unchanged with PUc concentration by keeping 0.8~0.9, and has no scattering dependence, suggesting the assembly of PUc/P4VP is spherical solid.

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