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Preparation and Size Determination of a Soluble Cross-Linked Macromolecule of Polyurethane with an Ethylene Diamine Chain Extender

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ABSTRACT: Transmission electron microscopy (TEM) pictures show that the intramolecularly cross-linked macromlecules (ICMs) have two kinds of networks: the “chemical network” and the “mechanical network”. The “chemical network” depends on the reactants and the feed ratio; the “mechanical network” is formed by the globules that are formed in the earlier stage of polymerization. The TEM pictures show that the morphologies of ICMs differ greatly from each other; the molecular size reaches hundreds of nanometers. It was found that the size of ICM with a high degree of cross-linking almost remains constant after the sample was dissolved, based on which we calculated the number-averaged molecular weight (M_n) of sample 1568EA-0.25, $M_n = 2.91 \times 10^8$.

1. Introduction

Microgels are of great interest and importance to many industrial disciplines such as components of binders for organic coatings, carriers of dyes, pharmaceuticals and biochemical compounds, and fillers and materials for reinforcing plastics. They were defined as intramolecularly cross-linked macromolecules by Funker in 1993.[1] During the past few decades, extensive efforts have been underway to synthesize ICM.[2−16] To understand the properties of ICM, it is important and necessary to investigate its solution behavior. ICM is clearly characterized by a 3-d network structure, which is more complex than that of linear, branched, star, combed, and cycled macromolecules. These five types of macromolecules all exhibit plain zigzag structures when fully stretched out, while ICM does not. Therefore, ICM must have complicated properties and special functions. During the size determination process of ICM, we discovered that the ICMs tend to form molecular clusters (MCs) in solution, and the MCs-forming ability strongly depends on the degree of cross-linking.[17,18] ICM with a high degree of cross-linking cannot exist as single molecule until the concentration of ICM is diluted to 10^{-6} g/mL.[19] As time goes on, the particle size changes complicatedly. But in the long run, it decreases greatly, indicating that the MCs-forming ability decreases greatly as time goes on.

The TEM pictures show most ICMs are composed of stable-shaped globules with an average particle size of 20−30 nm, which we did not know before. It can be deduced that the globules are formed in the early stage of the polymerization, and then the reaction of the reactive groups on the globule surfaces produces a network of submicroscopic scale with two structures: a necklacelike structure and grapelike structure, called the “mechanical network” in this paper. The necklacelike structure is relatively loose and simple, while the grapelike structure is compact and complex. There is another kind of network of microscopic scale in the globules that is directly formed by molecular strands, called the “chemical network” in this paper. It is these two kinds of networks that lead to the strange solution behavior of ICM.

2. Experimental Section

2.1. Materials. Poly(oxytetramethylene) glycol (PTMG; M_n 1568) was prepared in our laboratory.[20] Diphenylmethane 4,4′-diisocyanate (MDI; Wanhua Co., Yantai, PRC), ethylenediamine (EA; the First Plant of Chemical Reagent, Tianjin, PRC) and *N*,*N*-dimethylformamide (DMF; the First Plant of Chemical Reagent, Tianjin, PRC) were purified by low-pressure distillation prior to use.

2.2. Polymerization. Into a four-neck flask equipped with a stir bar, reflux condenser, and N_2 on command was added 11.20 g of MDI, which was melted at 60 °C. Then 35.00 g of PTMG was slowly added dropwise and maintained at 60 °C for 45 min. The reaction mixture was then cooled to room temperature, and 150 mL of DMF and EA (0.66, 0.46, 0.33, and 0.16 g for the four samples, respectively) were added. The reaction was then allowed to stir at room temperature for 0.5 h, after which it was warmed to 80 °C and stirred for an additional 4 h. The mixture was then poured into a mold to remove the solvent. After evaporation of the solvent, the sample was dried to a constant weight at 70 °C under vacuum.

In this paper, the samples are denominated as 1568EA-1, 1568EA-0.7, 1568EA-0.5, and 1568EA-0.25, 1568 is the number-averaged molecular weight of PTMG, EA is ethylenediamine, and the numbers 1, 0.7, 0.5, 0.25 are the molar ratios of amine H atom in EA to the NCO group in the oligmer formed in reaction 1.

2.3. Molecule Size. Average particle sizes were monitored with a photon correlation spectrometer (PCS) using a BI-900-AT Correlator, a BI-200-SM Photometer, and an Innova 304 argon laser (wavelength in a vacuum $\lambda = 514.5$ nm). The system was operated at a scattering angle of 90°, a laser intensity below 200 mW, and a temperature of 298 K.

The dust in solution was removed by ultracentrifugation just before particle size measurement.[21] The details of PCS can be found elsewhere.[22−24] The results are shown in Tables 1−4.

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Table 1. Particle Sizes of 1568EA-1 at Different Concentrations and Different Times

	no. I-1[b] (2.12 × 10^{-3} g/mL)	no. I-2 (2.12 × 10^{-4} g/mL)	no. I-3 (2.12 × 10^{-5} g/mL)	no. I-4 (2.12 × 10^{-6} g/mL)
		Part 1 (1st Day)		
particle diam (nm)	613	472	296	174
	642	473	280	172
	674	487	283	172
	670	477	285	173
AE (nm)	650	477	286	173
RE (nm)	61	15	16	2
		Part 2 (9th Day)		
particle diam (nm)	446	319	275	247
	469	312	259	236
	508	304	265	237
	504	303	267	233
AE (nm)	482	310	267	238
RE (nm)	62	16	16	14
		Part 3 (19th Day)		
particle diam (nm)	776	492	269	235
	763	503	278	246
AE (nm)	770	498	274	241
RE (nm)	13	11	9	11
		Part 4 (45th Day)		
particle diam (nm)	669	*e*	*e*	258
	689	*e*	*e*	243
AE (nm)	679			251
RE (nm)	20			15

[a] In Tables 2, 3, and 4, RE and AE are processed in the same way. [b] The Roman numeral represents the serial number of the sample, and the Arabic numeral represents the serial number of the solution. [c] The average number of the readings. [d] The difference between the maximum and minimum readings. [e] The particle size is not determined at this concentration.

Table 2. Particle Sizes of 1568EA-0.7 at Different Concentrations and Different Times

	no. II-1 (1.91 × 10^{-3} g/mL)	no. II-2 (1.91 × 10^{-4} g/mL)	no. II-3 (1.91 × 10^{-5} g/mL)	no. II-4 1.91 × 10^{-6} g/mL)
		Part 1 (1st Day)		
particle diam (nm)	1219	564	169	253
	1182	551	164	246
	1203	520	157	234
	1155	559	158	240
AE (nm)	1190	549	162	243
RE (nm)	64	44	12	19
		Part 2 (2nd Day)		
particle diam (nm)	1130	554	165	301
	1131	581	160	295
	1139	565	154	291
	1056	567	160	284
AE (nm)	1114	567	160	293
RE (nm)	83	27	11	17
		Part 3 (4th Day)		
particle diam (nm)	1144	593	165	318
	1048	576	162	319
AE (nm)	1096	585	164	319
RE (nm)	96	17	3	1
		Part 4 (17th Day)		
particle diam (nm)	923	563	157	330
	889	568	159	353
AE (nm)	906	566	158	342
RE (nm)	34	5	2	23
		Part 5 (29th Day)		
particle diam (nm)	981	549	162	369
	988	552	167	388
AE (nm)	985	551	165	379
RE (nm)	7	3	5	19

2.4. Transmission Electron Microscopy. Droplets of DMF solutions (10^{-6}g/mL) containing ICMs were placed onto carbon-coated copper grids (400 mesh). The solvent was evaporated in air for 12 h. Electron micrographs were taken on a Philips T20ST Transmission electron microscope at an acceleration voltage of 200 kV.

2.5. The determination of Swelling Ratio of Sample 1568EA-0.25. A solid sample of 1568EA-0.25 was cut into two rectangles of approximately 4 mm in length, 2 mm in width, and 2 mm in height. We accurately measured the length, width, and height of each rectangular section using a micrometer. The sections were soaked in DMF and then allowed to stand for 24 h at 60 °C, then 3 h at 100 °C, and then 3 h at 120 °C, respectively. We then accurately measured the length, width, and height of each rectangular section at each temperature using the micrometer. The experimental results are shown in Table 5.

3. Results and Discussion

3.1. .Synthesis of ICMs. 3.1.1. Controlled Cross-Linking Polymerization. The main reactions are shown in Scheme 1.

Table 3. Particle Sizes of 1568EA-0.5 at Different Concentrations and Different Times

	no. III-1 (1.88 × 10^{-3} g/mL)	no. III-2 (1.88 × 10^{-4} g/mL)	no. III-3 (1.88 × 10^{-5} g/mL)	no. III-4 (1.88 × 10^{-6} g/mL)
Part 1 (1st Day)				
particle diam (nm)	578	278	629	225
	584	258	636	220
	571	262	652	209
	572	258	711	215
AE (nm)	576	264	657	217
RE (nm)	13	20	82	16
Part 2 (8th Day)				
particle diam (nm)	553	269	651	222
	618	266	620	214
AE (nm)	586	268	636	218
RE (nm)	65	3	31	8
Part 3 (15th Day)				
particle diam (nm)	615	308	667	221
	570	293	683	225
AE (nm)	593	301	675	223
RE (nm)	45	15	16	4
Part 4 (31st Day)				
particle diam (nm)	537	321	639	230
	527	317	681	224
AE (nm)	532	319	660	227
RE (nm)	10	4	42	6

Table 4. Particle Sizes of 1568EA-0.25 at Different Concentrations and Different Times

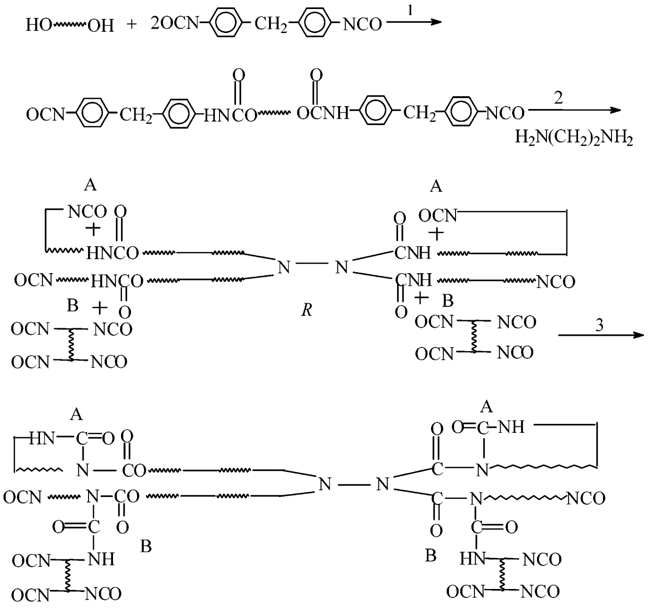
	no. IV-1 (2.02 × 10^{-3} g/mol)	IV-2 (2.02 × 10^{-4} g/mol)	IV-3 (2.02 × 10^{-5} g/mol)	IV-4 (2.02 × 10^{-6} g/mol)
Part 1 (1st Day)				
	541	771	262	193
particle diam (nm)	556	762	257	187
	536	711	248	184
	544	740	254	184
AE (nm)	544	746	255	187
RE (nm)	20	60	14	9
Part 2 (4th Day)				
particle diam (nm)	510	728	263	191
	510	758	254	191
AE (nm)	510	743	259	191
RE (nm)	0	30	9	0
Part 3 (24th Day)				
particle diam (nm)	499	775	272	249
	507	747	281	238
AE (nm)	503	761	277	244
RE (nm)	8	28	9	11
Part 4 (31st Day)				
particle diam (nm)	544	794	292	204
	506	758	331	212
AE (nm)	525	776	312	208
RE (nm)	38	36	39	8

Table 5. Swelling Ratios of Two Pieces of Sample 1568EA-0.25 at Different Temperatures

no.	temp (°C)	soaking time (h)	length (mm)	width (mm)	height (mm)	vol (mm^3)	swelling ratio (*Q*)
1	room temp	0	4.12	2.32	0.2	1.91	1
	60	24	7.9	4.31	0.4	13.61	7.12
	100	3	7.8	4.42	0.4	13.79	7.22
	120	1	dissolved				
2	room temp	0	3.61	1.87	0.2	1.35	1
	60	24	7.17	3.47	0.4	9.95	7.37
	100	3	7.20	3.57	0.4	10.16	7.53
	120	1	dissolved				

The oligomer capped with NCO is formed by reaction 1,[17,18] and the chain extension step is shown in reaction 2. In this step, reducing the amount of the chain extender leads to the formation of NCO-terminated prepolymer R. The rest of the remaining NCO groups can react with the H atoms of −NHCOO- and $-N(CONH)_2$ groups to result in the cross-linking of prepolymer.[18,19] Reactive site A can allow for consequential intramolecular conjugation. It is an intramolecular reaction, which does not increase the molecular weight of the ICM. Reactive site B can allow for consequential intermolecular conjugation. It is an intermolecular reaction, which increases the molecular weight of the ICM. If it is not controlled, an insoluble and infusible cross-linked polymer will be obtained. When a great amount of reactive functional groups were consumed by intramolecular reaction and the concentration of the reactive groups on coil surface is below the critical level to permit further intermolecular reaction, a soluble ICM is synthesized.[25]

Scheme 1. Reactions in the Polymerization System



3.1.2. The "Mechanical Network" and the "Chemical Network" in ICM. Each of the TEM pictures in Figure 1 shows an ICM with a clear there-dimensional morphology that does not collapse when the solvent is removed. ICMs comprise globules with a well-defined and stable internal structure. It can be inferred that the globules were formed in the early stage of polymerization, and then the reaction of the functional groups on the globule surface produces ICM with different morphologies. It is the intramolecular reaction (reaction 3) that results in the stable shape of the globule.

The globules of ICM in Figure 1a exhibit good dimensional uniformity, and their sizes range from 20 to 30 nm. They link hand in hand to form a necklacelike ICM with a simple structure.

Figure 1b shows a grapelike ICM which contains a large number of globules with a relatively wide size dispersity; the sizes of globules range from 10 to 40 nm. These interior compartments that are connected through urethane linkages accumulate so compactly that the electron beam can hardly penetrate the ICM. From the shade of the gray used, it can be seen that the distribution of the globules is skewed. There are more globules having a dark shade of gray than those having a light shade of gray.

ICM in Figure 1g has a very simple structure containing only two globules with a diameter of about 400 nm. Analogously, ICMs in Figure 1, parts d, e, and f, are composed of a small quantity of globules with a relatively big size.

A network at submicroscopic scale is formed by the globules, called the "mechanical network" in this paper, while the molecular strands connect to each other to

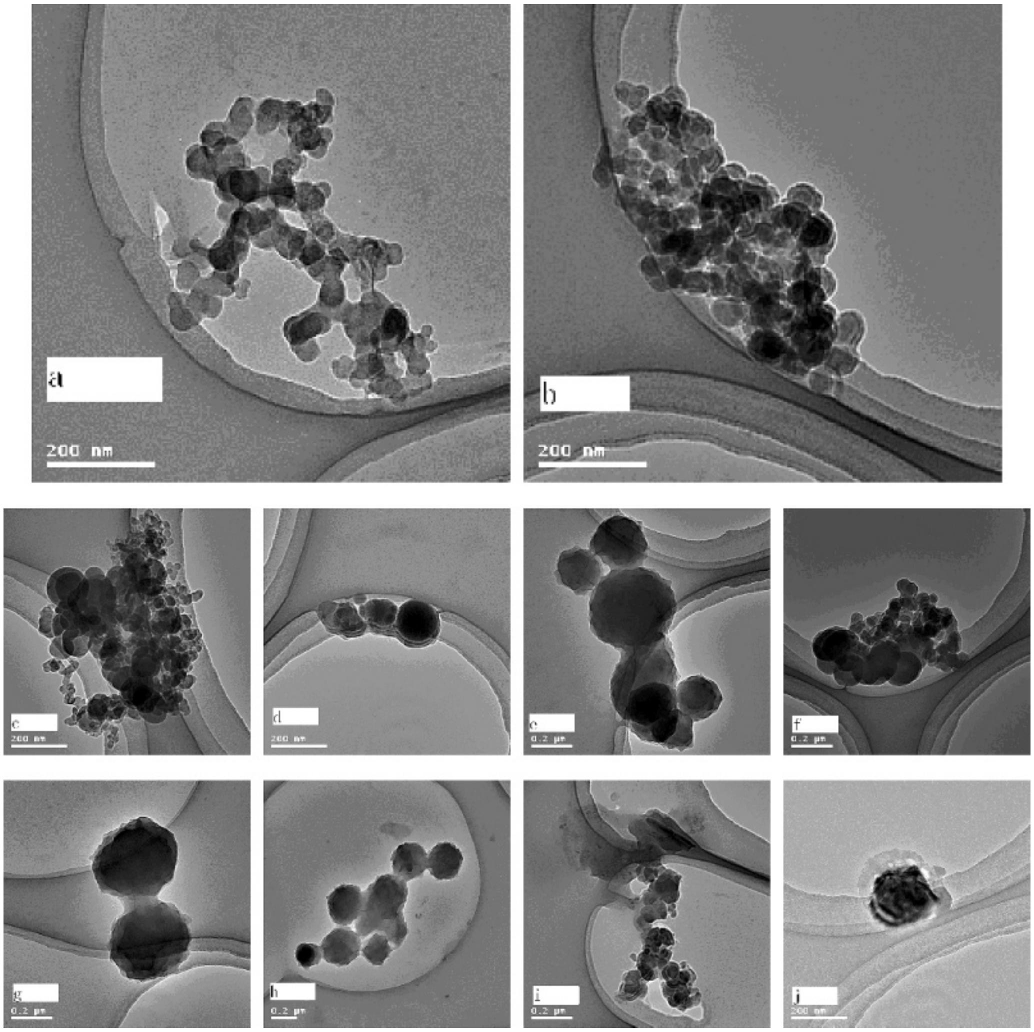


Figure 1. TEM pictures of ICMs of sample 1568EA-0.25 Pictures a–j are 10 TEM pictures of ICMs of sample 1568EA-0.25.

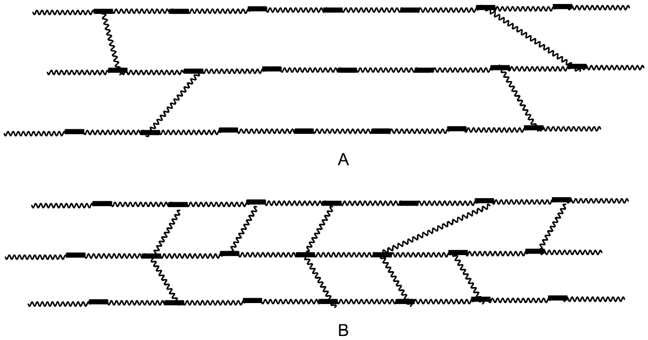


Figure 2. Schematic representation of the "chemical network": (A) the "chemical network"of ICM with a low degree of cross-linking; (B) the "chemical network" of ICM with a high degree of cross-linking.

result in a network at microscopic scale, which is called the "chemical network" in this paper.

The "mechanical network" of ICM in Figure 1a has a necklacelike structure, the diameter of one of the loops reaches 100 nm. ICM in Figure 1b has a grapelike structure which is a little dense that we cannot see big meshes. The globules in parts d, e, g, and h of Figure 1 are too few to form the "mechanical network". The globules in Figure 1c connect to each other to form a big rectangular mesh.

The "chemical network" is directly formed by the reaction of the monomer. Its density depends on the feed ratio, the more the amount of EA, the higher the degree of the cross-linking, and the denser the "chemical network". The "chemical networks" with a low and high degree of cross-linking are shown in Figure 2.

3.1.3. Analysis of the Degree of Cross-Linking. Assuming that two of the amine H atoms of a diamine participate in the formation of macromolecular chain, just like the hydroxyl H atoms of glycol in the polymerization with a glycol chain extender, the other two amine H atoms participate in the branching reaction. In reaction 2, if the ratio of amine H atoms of diamine to $-$NCO groups in the oligomer is 1:1, reaction 3 will not occur. Therefore, the amine H atoms participating in the branching reaction share 50% of the total amount of amine H atoms. The degree of cross-linking (DC) can be calculated by eq 4.

$$\mathrm{DC} = \frac{\frac{1}{2}}{1} \times 100\% = 50\% \tag{4}$$

If the decrease fraction of diamine is p %, the ratio of amine H atoms of the diamine to the $-$NCO groups of the oligomer is (1 $-$ p %):1. After reaction 2, the remained $-$NCO groups of the prepolymer R will participate in reaction 3 and develop branch points. Then the degree of cross-linking can be calculated by eq 5.

$$\mathrm{DC} = \frac{\frac{1 - p\ \%}{2} + p\ \%}{1} = \frac{1 + p\ \%}{2} \tag{5}$$

In the polymerization system with a glycol chain extender, when the amount of the glycol is equal to that of the oligmer, in theory, the degree of cross-linking is zero. When the amount of the glycol is less than that of the oligmer, branching points will be produced. Therefore, the decrease fraction of the glycol (p %) is the degree of cross-linking, shown in eq 6.[19]

$$\mathrm{DC} = \frac{p\ \%}{1} = p\ \% \tag{6}$$

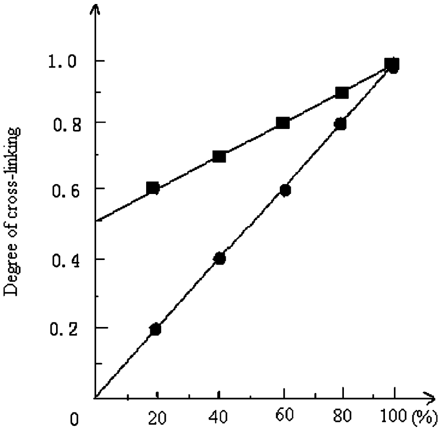


Figure 3. Variation of the degree of cross-linking with the decrease fraction of chain extender: (■) cross-linking polymerization system with a diamine chain extender; (●) cross-linking polymerization system with a glycol chain extender.

Degree of cross-linking was plotted vs the decrease fraction of chain extender according to eqs 5 and 6, shown in Figure 3.

3.1.4. Viscosity of the Reaction Mixture. The viscosity of the reaction mixture is very high because of the huge size of ICM. The amount of EA has a very significant influence on the viscosity, the less the amount of EA, the huger the size of ICM, and the higher the viscosity of the reaction mixture. In the polymerization where the decrease fraction of EA is 30% or more, the phenomenon of rod-climbing (Weissenberg effect) can be observed when the reaction was carried out for about 0.5 h at 80°C, followed by gelation. The resulting mixture is always mistaken for an insoluble and infusible material. In fact, it can be dissolved by adding DMF, heating to 120$-$150°C, and letting mixture stand for a few minutes.

3.2. Molecular Sizing. 3.2.1. The Preparation of the Sample Solution. The dissolving rate of the sample differs greatly from each other. Sample 1568EA-1 was dissolved quickly at 60 to 70 °C, while sample 1568EA-0.25 was dissolved slowly at 140$-$150 °C with strong stirring, indicating that ICMs of sample 1568EA-0.25 aggregated more tightly in the solid than that of sample 1568EA-1. If ultracentrifugation was carried out immediately after sample 1568EA-0.25 was dissolved, we can see a low scattering intensity during the size determination process, indicating that the dissolution of the sample was incomplete and there were "microcrystal" (very huge MCs) in solution. However, we can see a strong scattering intensity during the size determination process if ultracentrifugation was carried out 4 days after this sample was dissolved, indicating that the dissolution was completed. Therefore, to ensure that the dissolution was complete, the particle sizes were determined 4 days after all the samples were dissolved, and the 1st day in the following tables means the 1st day when the particle size determination was made.

3.2.2. The Strange Solution Behavior of ICM. From Tables 1$-$4, it can be seen that the particle sizes have two characteristics. 1. The particle size cannot be repeated. 2. The particle size decreases with decreasing

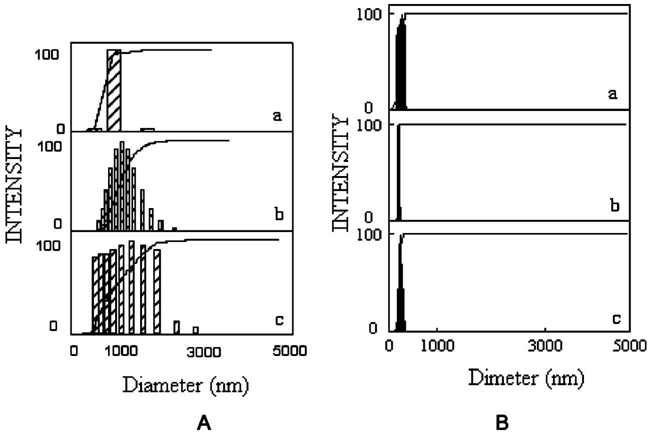


Figure 4. Particle diameter distribution obtained by CONTAIN analysis of samples of 1568EA-0.7 at different times: (A) Particle diameter distribution of solution no. II-1 at different times; (B) Particle diameter distribution of solution no. II-4 at different times.

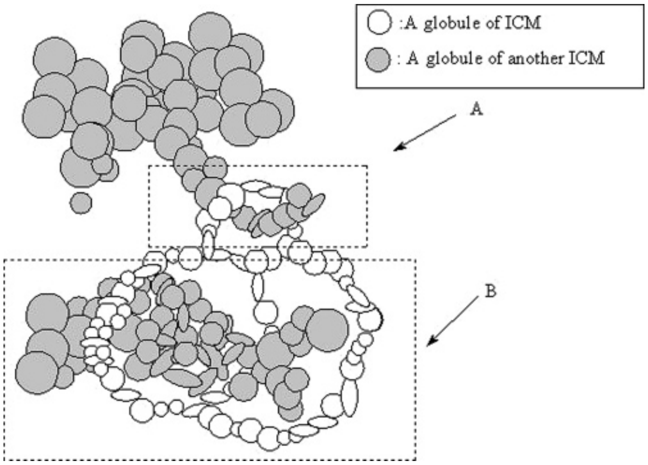


Figure 5. Schematc representation of the aggregation between ICMs: (○) a globule of ICM; (●) a globule of another ICM

the concentration of ICM. It is indicated that ICMs tend to form MCs in solution and the formation and dissociation of the MC is in a nonequilibrium state. Graph A in Figure 4 shows that the particle sizes in solution no. II-1 are very huge and wide-distributive and change greatly as time goes on. Graph B in Figure 4 shows that the particle sizes in solution no. II-4 are relatively small and narrow-distributive and almost remain constant as time goes on. It can be deduced that ICMs exist mainly as MCs in solution no. II-1, while they exist mainly as single molecules in solution no. II-4. We have discussed this issue in detail in the literature.[19]

The TEM pictures in Figure 1 provide new proofs of the above experimental results. An ICM could be caught by the mesh of the “mechanical network” of another ICM when they collided with each other, shown in Figure 5.

Graph A in Figure 5 shows that a small part of an ICM is caught by a mesh of the “mechanical network” of another ICM; Graph B in Figure 5 shows that a large part of ICM is caught by the “mechanical network” of another ICM. The aggregation is not so strong that it can be destroyed under the solvation effect and the movement of ICM itself. Because the shape of ICM and the topology of the “mechanical network” are irregular, the interactions between ICMs are arbitrary. Therefore, the formation and dissociation of the MC is in a noneqilibrium state. The “chemical network” also has influence on the formation of MCs, which we have discussed in detail in the literature.[19] The aggregation between ICMs is described as “biting” in the literature.[19] The reseau of the “chemical network” in ICM is just like a mouth, when a “tongue” of another ICM (the segments of another ICM) enters the reseau, it can be bitten tightly, a MC is then formed. The biting ability of the reseau strongly depends on the degree of cross-linking of ICM. On one hand, the higher the degree of cross-linking, the stronger the biting ability of ICM will be. On the other hand, the softer the “tongue”, the easier it is to be bitten.

3.2.3. The Influence of the Amount of Chain Extender and Concentration of ICM on the Particle Size. Each of Tables 1−4 is divided into several parts: part 1 shows the data determined on the 1st day, the other parts show the data measured on following days. Data in part 1 are discussed in this section. It can be seen from the tables that with decreasing the amount of chain extender, AE of solution no. 1 rises first, and then falls. For example, AEs of nos. I-1, II-1, III-1, and IV-1 are 650, 1190, 576, and 544 nm, respectively. This issue has been discussed in detail in the literature.[19]

AEs change complicatedly with the concentration of ICM. For the samples with a low degree of cross-linking, AEs decrease monotonically with decreasing the concentration of ICM, but it is not the case for the samples with a high degree of cross-linking. For example, with decreasing concentration of ICM, AE of sample 1568EA-0.5 decreases first, and then increases, and then decreases again. However, with decreasing concentration of ICM, AE of sample 1568EA-0.25 increases first, and then decreases. The concentration dependence of AE changes greatly with the degree of cross-linking of ICM. ICM with a mild degree of cross-linking tends to swell with decreasing the concentration of ICM, resulting in an increase in its MC-forming ability. Therefore, we can see a fluctuation in the particle size of sample with a mild degree of cross-linking with the decrease in the concentration of ICM.

3.2.4. The Time Dependence of Particle Size. By comparing parts 1 and 2 in Table 1, we can see that as time goes on AEs in solution nos. I-1 and I-2 decrease, AE in solution I-3 almost remains constant, while AE in solution I-4 increases. ICMs synthesized in this paper are multiblock copolymers with a distribution of hard- and soft-segment blocks. The hard and soft phases tend to segregate due to their immiscibility, and produce a phase-separated morphology of hard-segment-rich and soft-segment-rich phases that are connected through urethane linkages. The thermodynamic driving force for minimizing the total free energy of the system results in preferential surface segregation of the lower surface energy constituent (soft-segment block) of the polymer.[26,27] On one hand, when the hard segments are covered by the soft-segment-rich phases, MCs-forming ability will be decreased. On the other hand, the association of hard segments acting as physical cross-links leads to a shrunken volume of ICM and then decreases the size of MC.

AE in part 2 of solution no. I-4 (238 nm) is bigger than that in part 1 (173 nm). This might because the topology of network in ICM is irregular. The region with a high cross-link density in ICM swells slowly as time goes on. Therefore, we can see a larger AE in part 2 than in part 1.

The particle sizes in solution no. II-4 increase monotonically as time goes on. Sample 1568EA-0.7 has a higher degree of cross-linking (65%) than sample 1568EA-1 (50%), therefore, the swelling rate of sample 1568EA-0.7 is slower than that of 1568EA-1, and it takes more time for the ICM of sample 1568EA-0.7 to reach its swelling limit compared with sample 1568EA-1. AEs in solution nos. III-4 and IV-4 do not increase as time goes on, which might because the swelling rates of these two samples are too slow to be observed on the experimental time scale.

The ICMs in solution nos. II-3 and II-4 exist as single molecules, and the single molecular size of ICM in solution no. II-4 is larger than that in no. II-3. This might because the collision frequency between ICMs in solution no. II-3 is bigger than that in no. II-4. Researches [28,29,30] reported that the collision between macromolecules can inhibit their swelling. ICM in solution no. II-3 has a higher collision frequency compared with solution no. II-4; therefore, the single molecular size in solution no. II-3 is relatively small.

Researches on the viscosity of linear macromolecules in solution in the 1950s[29,30] reported that the molecules will swell when the concentration of ICM falls to 10^{-4}g/mL, which is a "critical concentration". However, the "critical concentration" for sample 1568EA-0.7 is 10^{-6}g/mL. This indicates that the "critical concentration" of ICM is much lower than that of linear macromolecule.

4. The Calculation of Molecular Weight

Traditional methods for determining the molecular weight can hardly be applied to ICM because of its special structure and huge size. The molecular size of ICM can be accurately determined using PCS. The number-averaged molecular weight of soft segment (PTMG) of ICM in this paper is 1568. Even ICM with the highest degree of cross-linking can also swell in its good solvent because there are at least 88 C atoms and 22 H atoms between the cross-linking points. Therefore, the single molecular size determined by PCS is the size of swollen ICM. To get the single molecular size of ICM in solid materials, we must get the swelling ratio (Q) of ICM. The calculation is as follows:

$$\frac{\mathrm{V}_{\mathrm{s}}}{V_0} = \frac{V_{\mathrm{ms}}}{V_{\mathrm{m}}} = Q \tag{7}$$

V_{s}: the volume of the fully swollen solid sample

V_0: the volume of not-swollen solid sample

V_{ms}: the volume of the fully swollen ICM

V_{m}: the volume of ICM in solid sample

Q: the swelling ratio

Repeated experiments show that the sample with a high degree of cross-linking has two characteristics. 1. When immersed in its good solvent under a high temperature for a long time, it will not be dissolved, but swell. 2. The volume of ICM will remain constant after dissolved. Therefore, we can obtain its swelling ratio. The number-average molecular weight (M_{n}) is calculated by eq 8:

$$M_{\mathrm{n}} = V_{\mathrm{m}} d N_{\mathrm{A}} \tag{8}$$

M_{n}: the number-average molecular weight

d: the density of solid sample

N_{A}: Avogadro's number

Substituting eq 7 into eq 8, we can get eq 9:

$$M_{\mathrm{n}} = \frac{N_{\mathrm{A}} V_{\mathrm{ms}} d}{Q} \tag{9}$$

$$V_{\mathrm{ms}} = \frac{4}{3}\pi r^3 \tag{10}$$

r: the radius of ICM in solution = AE/2 (AE is in solution no. IV-4)

Then we can get the number-average molecular weight of ICM:

$$M_{\mathrm{n}} = \frac{4\pi r^3 N_A d}{3Q} \tag{11}$$

It can be seen from Table 5 that the swelling ratios of the two rectangular sections are 7.12 and 7.37 when the sections were immersed at 60 °C for 24 h, and 7.22 and 7.53 when immersed at 100 °C for 3 h. The swelling ratio of the samples at 60 °C is almost the same as that at 100 °C, indicating that the final swelling ratio does not depend on the temperature. The two sections were dissolved quickly in DMF at 120 °C. Therefore, the swelling ratio of the solid sample in DMF at 100 °C for 3 h is the final swelling ratio of ICM.

$$Q = \frac{7.22 + 7.53}{2} = 7.38$$

$$r = \frac{AE}{2} = \frac{187}{2} = 93.5 \text{ nm} \quad \text{(AE is in solution IV-4)}$$

$d = 1.0437$ g/cm^3
(the density determination process is omitted)

$$M_{\mathrm{n}} = 2.91 \times 10^8$$

5. Conclusions

1. TEM pictures show that there are two stages in the development of ICM. (a) The globules with well-defined and stable shapes were formed in the early stage of the polymerization. During this stage, the "chemical network" was formed by the reaction of the monomers. (b) Further reaction of the reactive groups on the globule surface produces ICM with different morphologies. During this stage, the "mechanical network" was formed.
2. As time goes on, the MCs-forming ability decreases greatly.
3. We calculate the number-averaged molecular weight of ICM with a high degree of cross-linking using its size.

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