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ABA Block Copolymers of Polytetrahydrofuran and Linear Polyethylenimine and Their Complexes with Copper Chloride

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ABSTRACT: Well-defined ABA block copolymers, in which A block is linear polyethylenimine (LPEI) and B block is polytetrahydrofuran (PTHF), have been synthesized by the hydrolysis of the corresponding poly(2-methyl-2-oxazoline) (PMeOx) containing block copolymers, which are obtained by sequential bifunctional living cationic ring-opening polymerization of THF and MeOx, initiated with trifluoromethanesulfonic acid anhydride. Addition of $CuCl_2$ to these block copolymers leads to the formation of the corresponding LPEI−$CuCl_2$ complexes, which resulted in dramatic changes in physical properties. Depending on the relative length of each block and on the ratio of [N]/[Cu], the complexed polymers were soft and ductile materials or tough thermoplastic elastomers.

Introduction

Ionomers, polymers containing a small amount of ionic groups, display dramatic changes in physicomechanical properties compared with the parent polymers which do not contain ionic groups due to the strong intermolecular interactions of ionic moieties.[1]

Telechelic ionomers,[2−4] in which the ionic groups are attached at each end of linear chains, are well-suited for structure−property analyses because the molecular weight, the functionality, and the placement of ionic groups can be clearly established. Block ionomers,[5−7] in which one of the blocks is ionic, have been reported to show a greater driving force for phase separation than nonionic systems.

Polymers “cross-linked” by coordination complexes may be considered as similar to ionomers, i.e., they show microphase separation and thermoreversibility of the cross-linking.[8,9] Thermoplastic elastomers could be obtained by complexation of ABA triblock and $(AB)_n$ multiblock copolymer systems with 6,6′-disubstituted 2,2′-bipyridine as block A and poly(oxytetramethylene) as soft segment B, with Cu(I) ions.[10] Recently, we described the thermoplastic materials with thermoreversible physical cross-links, consisting of high-melting poly(ethylene oxide)−sodium thiocyanate (PEO−NaSCN) complexes in a low-melting poly(tetrahydrofuran) (PTHF) matrix, formed by the complexation of triblock copolymers PEO−PTHF−PEO with NaSCN.[11]

It is well-known that linear polyethylenimine (LPEI) can form complexes with metal ions because the nitrogen atoms in the polymer act as electron donors.[12] Cu(II) ions, for example, form stable complexes having a four-coordinate planar structure.[13−14]

This study addressed the possibility to create, or enhance, the intermolecular forces between ABA block copolymer chains based on the block-specific complexation of the A blocks and hence to modify the physical properties of the copolymers upon complexation. This was achieved by complexing $CuCl_2$ with LPEI blocks situated at both sides of a flexible poly(tetrahydrofuran) (PTHF) chain middle block.

Experimental Section

Materials. Acetonitrile (Aldrich, 99%, CH_3CN), 2-methyl-2-oxazoline (Acros, 98%, MeOx) and morpholine (Baker, reagent grade) were purified by distillation over calcium hydride. Trifluoromethanesulfonic anhydride (Fluka, 97%, Tf_2O) was purified over phosphorus pentoxide. Tetrahydrofuran (Acros, 99%, THF) was dried over sodium wire. All operations were carried out under dry nitrogen. Copper dichloride (Aldrich, 99%, $CuCl_2$) was dried in a vacuum at 100 °C until constant weight.

Preparation of Block Copolymers LPEI−PTHF−LPEI. 1. Preparation of Triblock Copolymers PMeOx−PTHF−PMeOx (e.g., 10−190−10). With continuous stirring, 312 μL (1.85 mmol) of Tf_2O was added to 150 mL of dry THF (1.85 mol) at 25 °C under nitrogen. After 45 min, 3 mL of MeOx was added to terminate the polymerization of THF. Unreacted THF was removed by evaporating and replaced by 150 mL of CH_3CN. To this mixture was added 22.5 mL of MeOx (0.265 mol) and polymerization was continued at 70 °C for 2 h. The reaction was terminated by addition of 6 mL of morpholine. The polymer was precipitated in cold 0.1 N NaOH aqueous solution and filtered off, washed with water, and dried in a vacuum. The polymer was characterized by NMR (360 MHz Bruker FT-NMR spectrometer) and GPC (Waters 150-C gel permeation chromatography).

2. Hydrolysis of Block Copolymer PMeOx−PTHF−PMeOx (e.g., 10−190−10). A total of 25 g of block copolymer PMeOx−PTHF−PMeOx was dissolved in 190 mL of a mixture of methanol and water. After 60 mL of 37% hydrochloric acid was added, the solution was refluxed under nitrogen for 12 h. After cooling, the pH of the solution was adjusted to 9 with NaOH, and the precipitate was filtered off and washed with water until neutral. A total of 8 g of LPEI−PTHF−LPEI block copolymer was obtained.

Preparation of Cu Complexes of LPEI−PTHF−LPEI Block Copolymers. The block copolymers LPEI−PTHF−LPEI were dissolved in methanol to give solutions of about 0.1 mol/L (molar concentration of amino groups). Different amounts of $CuCl_2$ dissolved in methanol were added dropwise to this solution with stirring at room temperature. After the solvent was evaporated, the resulting samples were dried in a vacuum at 60 °C overnight.

Characterization of LPEI−PTHF−LPEI Block Copolymers and Their Cu Complexes. Thermal parameters of complexes (T_g, T_m, T_c, and ΔH_m) were determined by DSC, with

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a Perkin-Elmer DSC-7 data station. The measurements were carried out at a rate of 10 °C/min. First heating run was from −100 °C to 110 °C, the specimen was held at this temperature for 20 min, and cooled to −100 °C at the same rate. The second heating run started directly after 10 min cooling of the sample at −100 °C. The changes in heat of melting (ΔH_m) of the complexes were determined from the area of the corresponding transitions in the DSC scans.

Morphological characterization were performed under the Olympus model BH-2 polarizing optical microscope coupled to a hot stage TMS91 and the video system of TM-1500PS color video monitor and color video printer UP-3000P. The samples were prepared by solvent-casting. The samples were heated to 110 °C at the rate of 10 °C/min, held at 110 °C for 20 min, and then cooled to room temperature at the same rate. All optical microscopy photographs were taken after complete crystallization.

TGA was performed with a Polymer Laboratories thermogravimetric analyzer, PL-TGA.

A Polymer Laboratories dynamic mechanical analyzer, type PL-MKII equipped with temperature programmer was used in the temperature range below the melting temperature of PTHF. The samples were cut from the film molded by compression at 100 °C and 100 N in the size of 20 × 10 × 1 mm^3. A PHYSICA rheometer equipped with universal measuring drive system UM, rheometer electronic unit Rheolab MC20, and TCS laboratory temperature controller viscotherm TC5 with parallel-plate geometry was used in oscillation shear mode at higher temperatures. The test specimens with the thickness of ~1 mm and diameter of 25 mm were molded by compression at 100 °C and 100 N.

The elongation experiments were performed on a HT HounsField H10KM with a cell of 100 N. Dumbbell-shape specimens were cut from the film made by compression at 100 °C and 100 N.

Results and Discussion

Synthesis of Block Copolymers LPEI−PTHF−LPEI. Block copolymers LPEI−PTHF−LPEI were prepared by hydrolysis of the corresponding block copolymers PMeOx−PTHF−PMeOx, which were synthesized via cationic living polymerization using the sequential monomer addition method. First, THF was polymerized in bulk at 25 °C, with trifluoromethanesulfonic acid anhydride as initiator, to a well-defined bifunctional living polymer.[15] MeOx was then polymerized by the living ends of the first polymerization system to give the A blocks, which were terminated with morpholine, as described earlier.[16] In this way, a series of block copolymers, in which the central PTHF blocks had molecular weights ranging from 12 000 to 19 000 and the PMeOx blocks had molecular weights from 500 to 2000, were synthesized. These block copolymers were subjected to acid hydrolysis, by which the PMeOx segments were deacylated to form LPEI segments[12] without affecting the block structure. The overall reaction scheme is as shown in Scheme 1.

The degree of hydrolysis was determined from the integral ratio in the ^{1}H NMR spectra (Figure 1). It was higher than 95% in all cases. Several block copolymers in which LPEI blocks had molecular weights of 200 to 1000 were prepared. The compositions of the block copolymers are shown in Table 1.

Formation of Block Copolymer Complexes. Block copolymers LPEI−PTHF−LPEI were modified with $CuCl_2$ in the molar ratios of [N]/[Cu] = 16, 8, and 4. Blue complexes were formed in solution by mixing the solutions of polymer and copper salt. The products were obtained after evaporating the solvent. The compositions of the block copolymer complexes studied in this work are given in Table 2.

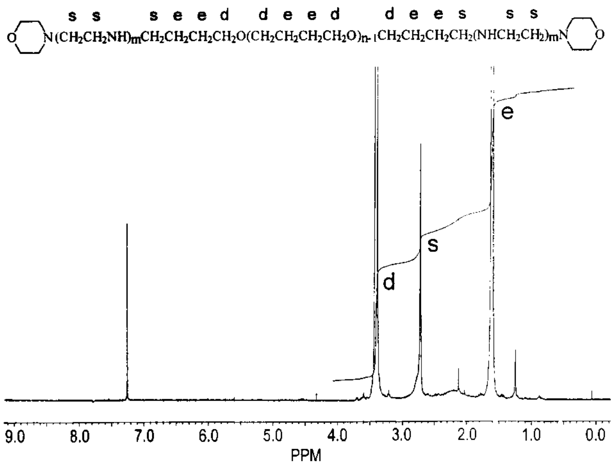
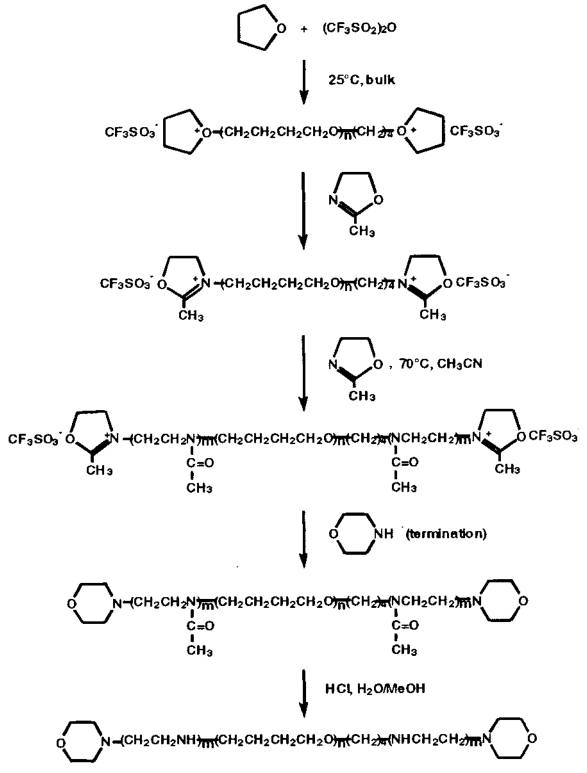


Figure 1. ^{1}H NMR spectrum (360 MHz) of block copolymer LPEI−PTHF−LPEI (H 10−120−10).

Scheme 1



Thermal Stability of Block Copolymer Complexes. Since one of the purposes of this project was to investigate the influence of complexation on the physical properties of the materials at different temperatures, it was important to evaluate the thermal stability of the ABA copolymers and their complexes. Figure 2 shows that the presence of $CuCl_2$ has a slight thermostabilizing effect on the block copolymer. However, this effect decreases with increasing $CuCl_2$ content.

Crystallization and Morphology of Block Copolymers and Their Complexes. Block copolymers LPEI−PTHF−LPEI are crystalline at room temperature due to the PTHF block. The LPEI blocks are not crystalline because of their low molecular weights. The glass transition temperature of LPEI was reported to be −23 °C.[12] The influence of complexation of the LPEI blocks on the crystallinity of the PTHF blocks was measured by DSC. As an example, Figure 3 shows the analysis of a pure block copolymer and of the same

Table 1. Synthesis of LPEI−PTHF−LPEI Block Copolymers

living PTHF[a]			PMeOx−PTHF−PMeOx[c]				LPEI−PTHF−LPEI[f]	
t (min)	M_n[b]	M_w/M_n[b]	sequence[h]	*t* (min)	M_n of each PMeOx[d]	M_w/M_n[e]	sequence[h]	M_n of each LPEI[g]
48	18 900	1.12	10−190−10	120	1130	1.34	H 5−190−5	565
43	15 600	1.10	10−160−10	120	1050	1.35	H 5−160−5	525
32	12 100	1.16	10−120−10	120	880	1.17	H 5−120−5	440
32	12 000	1.19	5−120−5	60	370	1.11	H 2−120−2	185
32	12 100	1.16	10−120−10	120	880	1.17	H 5−120−5	440
32	12 100	1.20	20−120−20	200	2230	1.20	H 10−120−10	1115

[a] Polymerization at 25 °C; [Tf_2O] = 0.012 mol/L. [b] Determined by GPC−RI: column, PL-Gel 10*μ* 10^3Å; eluent, THF; calibrated by polystyrene standards. [c] Polymerization at 70 °C, [MeOx] = 1.75 mol/L; solvent CH_3CN. [d] Calculated from ^1H NMR. [e] Determined by GPC−RI: column, Waters *μ*StyragelHT 10^3Å (10*μ*) + 10^4Å (10*μ*); eluent, NMP; calibrated by polystyrene standards. [f] A total of 12 h refluxing of PMeOx−PTHF−PMeOx; [HCl] = 8 mol/L; solvent H_2O/MeOH. [g] Calculated from M_n of PMeOx. [h] ABA block copolymer sequence with molecular weight, e.g. 10−190−10 stands for 1000−19000-1000.

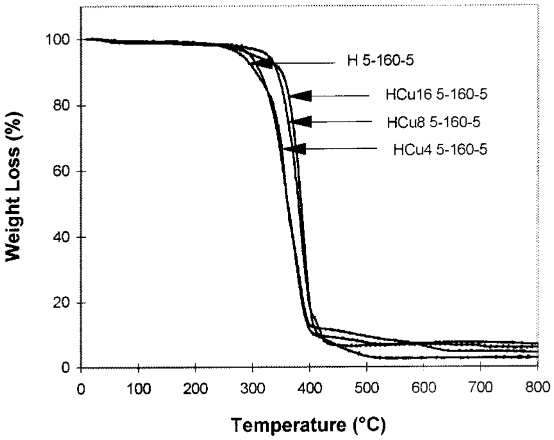


Figure 2. TGA curves of H 5−160−5 and its complexes with $CuCl_2$ (N_2; heating rate 10 °C/min).

Table 2. Complexation of Block Copolymers LPEI−PTHF−LPEI with $CuCl_2$

block copolymers	molar ratio of [N]/[Cu]	block copolymer complexes
H 5−160−5	16/1	HCu16 5−160−5
	8/1	HCu8 5−160−5
	4/1	HCu4 5−160−5
H 2−120−2		HCu4 2−120−2
H 5−120−5	4/1	HCu4 5−120−5
H 10−120−10		HCu4 10−120−10
H 5−190−5		HCu4 5−190−5
H 5−160−5	4/1	HCu4 5−160−5
H 5−120−5		HCu4 5−120−5

complexed with $CuCl_2$ ([N]/[Cu] = 4). Results of other DSC measurements are reported in Table 3.

It can be observed that the addition of $CuCl_2$ to block copolymers LPEI−PTHF−LPEI only slightly affects the melting temperature (from 31 to 29 °C) of the PTHF phase, but has a significant influence on its melt enthalpy (from 82 to 56 J/g). If the length of LPEI blocks is increased, the effect of complexation on the melting temperature becomes more important.

With the same molar ratio of [N]/[Cu] = 4 and the same molecular weight of LPEI (∼500), the crystallinity of block complexes increases with the decreasing of the length of B block PTHF. It has been reported earlier that the crystallinity of PTHF homopolymer with low molecular weight is higher than that of PTHF homopolymer with high molecular weight.[17]

Suppression of the crystallization of PTHF parts by the complexation of LPEI with $CuCl_2$ also can be seen in the optical microscopy. It was observed (Figure 4) that the typical Maltese cross in PTHF spherulites became unclear after complexation.

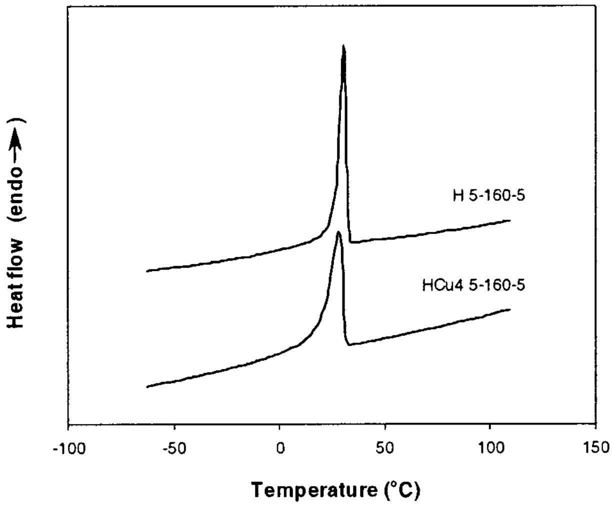


Figure 3. DSC traces of LPEI−PTHF−LPEI and its Cu complex (heating rate 10 °C/min).

Table 3. Melting and Crystallizing Transitions of Block Copolymer Complexes[a]

samples	T_m (°C)	ΔH_m (J/g_{PTHF})	T_c (°C)
H 5−160−5	31	82	4.8
HCu16 5−160−5	31	60	2.7
HCu8 5−160−5	30	66	2.9
HCu4 5−160−5	29	56	1.4
HCu4 2−120−2	33	82	2.2
HCu4 5−120−5	31	76	4.1
HCu4 10−120−10	27	52	3.1
HCu4 5−190−5	27	57	0.7
HCu4 5−160−5	29	56	1.4
HCu4 5−120−5	31	76	4.1

[a] Scanning range was −70 to 110 °C; scanning rate, 10 °C/min.

Dynamic Mechanical Properties of Block Copolymers and Their Complexes. When $CuCl_2$ is added to LPEI, the T_g of the material increases and the melt enthalpy of the crystalline fraction decreases. This is shown in Table 4.

In pure LPEI−PTHF−LPEI triblock copolymers, PTHF is crystalline and LPEI is amorphous. LPEI shows a glass transition temperature around −23 °C, which is indicated by a maximum of tan *δ* in the DMTA (Figure 5). After complexation of the block copolymers with $CuCl_2$, the T_g corresponding to the LPEI segments shifts to higher temperature, as expected from the results obtained with the homopolymer. With molar ratio [N]/[Cu] = 16, the T_g of LPEI remains essentially unchanged. Doubling the content of copper to [N]/[Cu] = 8, the T_g appears at ∼15 °C. When the molar ratio of

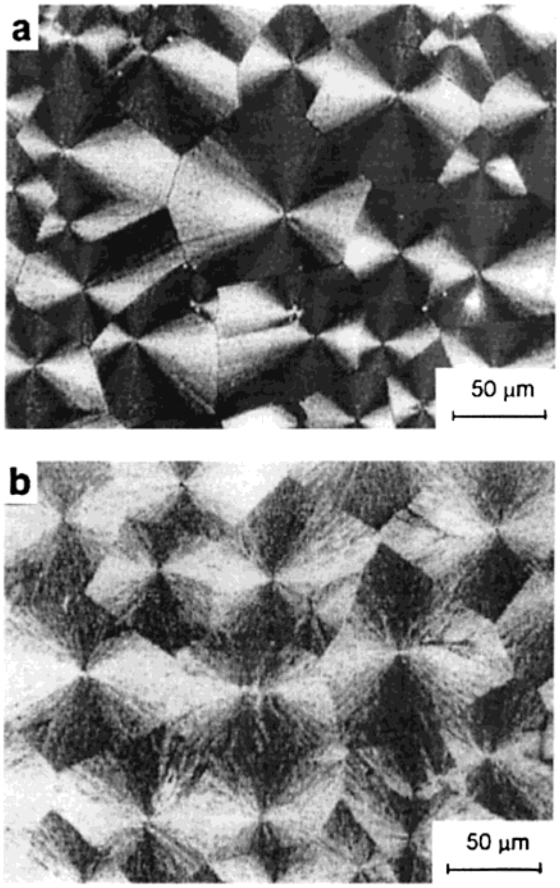


Figure 4. Polarized light microscopy photographs of block copolymer LPEI−PTHF−LPEI and its Cu complex: (a) H 5−16−5 and (b) HCu4 5−160−5.

Table 4. Thermal Transitions of LPEI and LPEI−Cu Complexes from DSC[a]

samples	T_m (°C)	ΔH_m (J/g_{LPEI})	T_g (°C)
LPEI	54	132	
N−Cu 32/1	55	71	−28
N−Cu 16/1	52	0.04	19
N−Cu 8/1			30
N−Cu 4/1			62

[a] Scanning run was from −100 to 110 °C; scanning rate; 10 °C/min; MW_{LPEI} = 2700.

[N]/[Cu] = 4, the T_g of the Cu complex shifts to ~30 °C.

Figure 6 shows the dependence of the shear storage modulus on temperature for the block copolymer H 5−160−5 and a series of complexes with different $CuCl_2$ contents. In the absence of copper salt, the storage modulus of the block copolymer H 5−160−5 drops to a low value immediately after the melting of the crystalline PTHF fraction around 40 °C. In the presence of copper salt, the flow is delayed and a rubbery plateau can be observed. With increasing copper salt concentration, the modulus of the complexed copolymers increases and the rubbery plateau extends to higher temperatures.

The effect of the molecular weight of the complexing LPEI block in the parent triblock copolymers on the modulus−temperature curves is shown in Figure 7. A molecular weight of LPEI blocks of 185 is not high enough to create strong physical associations so that the rubbery plateau is absent. When the molecular weight of the LPEI blocks is 1115, the storage modulus goes down a little after melting of the PTHF block and the rubbery plateau with a storage modulus > 10^5 Pa extends to 250 °C. That means there exists strong association due to the complexation.

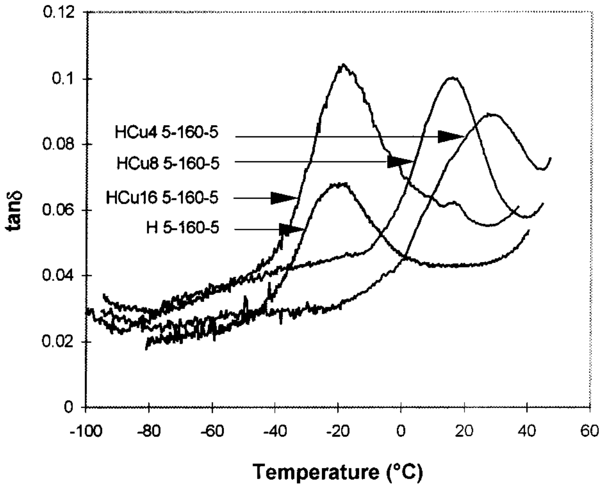


Figure 5. Temperature dependence of loss factor for H 5−160−5 and its Cu complexes with different molar ratio of [N]/[Cu] (f = 1 Hz; heating rate 3 °C/min).

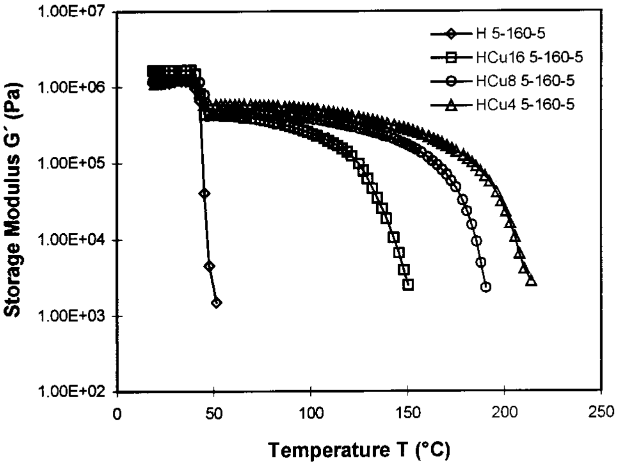


Figure 6. Temperature dependence of shear storage modulus for H 5−160−5 and its Cu complexes at different molar ratio of [N]/[Cu] (f = 0.5 Hz; heating rate 5 °C/min).

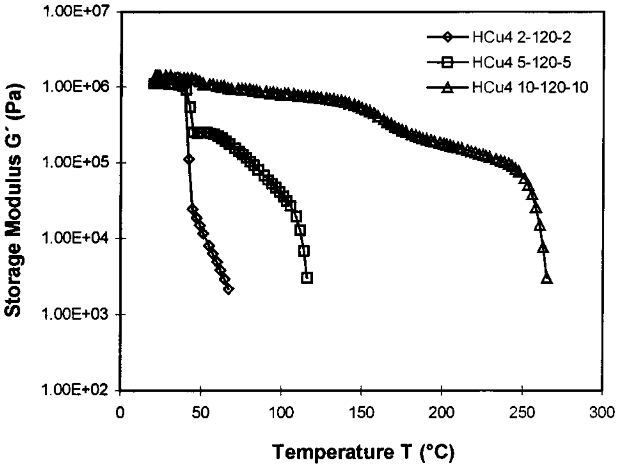


Figure 7. Temperature dependence of shear storage modulus for the block copolymer complexes with different lengths of A blocks (MW of PTHF ~12 000; [N]/[Cu] = 4; f = 0.5 Hz; heating rate 5 °C/min).

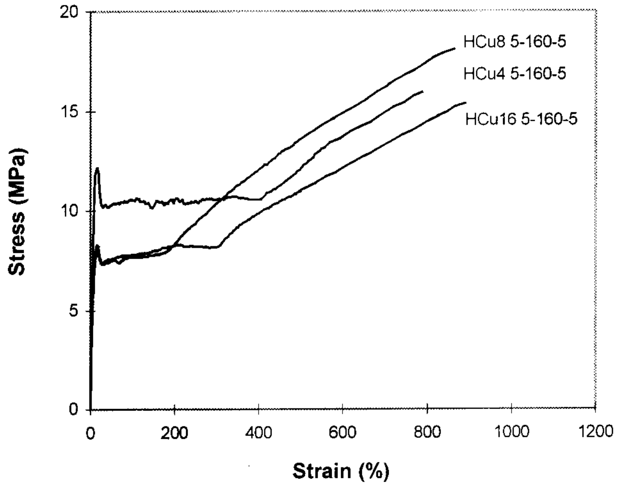


Figure 8. Stress–strain curves of block copolymer complexes at different molar ratio of [N]/[Cu] (H 5–160–5; 20 mm/min; 22 °C).

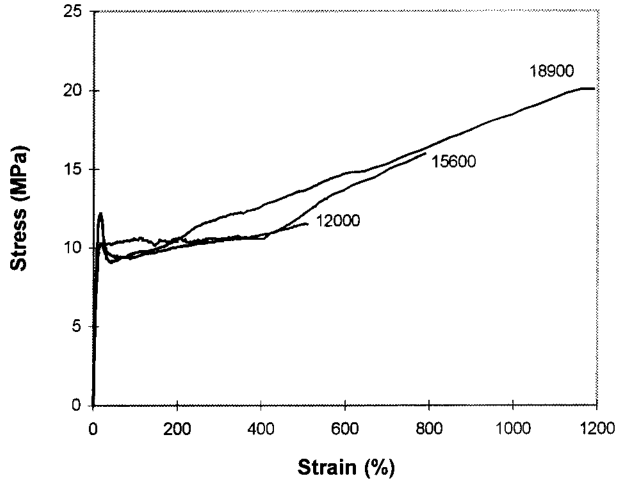


Figure 9. Stress–strain curves of block copolymer complexes with different MW of PTHF block (MW of LPEI ~450; [N]/[Cu] = 4; 22 °C; 20 mm/min).

Tensile Mechanical Properties of Block Copolymer Complexes. At room temperature, pure LPEI–PTHF–LPEI copolymers are brittle materials, whose stress–strain curves show only a few percentage points of elongation. By addition of $CuCl_2$, mechanical properties are dramatically changed. Figure 8 shows the stress–strain curves of block complexes with different [N]/[Cu] ratios at room temperature. All samples exhibit a maximum elongation of about 800%. The materials have a relatively high initial modulus which is ascribed to stress-induced crystallization of the PTHF segments at 22 °C.

The effect of molecular weight of the PTHF and LPEI segments on the stress–strain behavior of the materials is shown in Figures 9 and 10. By keeping [N]/[Cu] = 4 and changing the molecular weight of the central PTHF block, both tensile strength and elongation were observed to increase with increasing molecular weight of PTHF.

Figure 10 shows the stress–strain behavior of block complexes with different length of LPEI blocks. When the molecular weight of LPEI increases from 185 to 440, the material becomes ductile instead of brittle. However, when the molecular weight of LPEI is increased to 1115, the characteristics of cross-linking appear; that is, the elongation decreases but the tensile strength increases markedly. In this case, the polymer displays a higher modulus and higher stress values. Higher molecular weight LPEI leads to a higher cross-link density and consequently to a higher stiffness of the material.

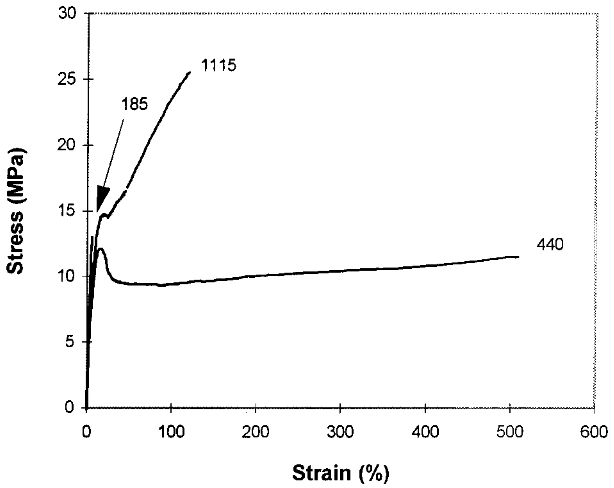


Figure 10. Stress–strain curves of block copolymer complexes with different length of LPEI blocks at 22 °C (MW of PTHF ~12 000; [N]/[Cu] = 4; 20 mm/min).

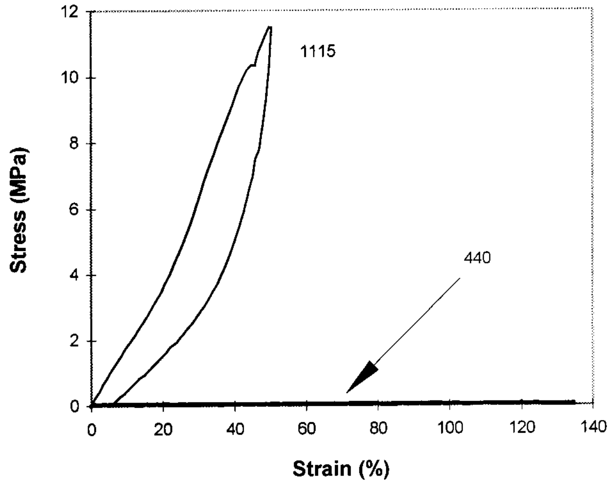


Figure 11. Hysteresis curves of block copolymer complexes with different length of LPEI blocks at 60 °C (MW of PTHF ~12 000; [N]/[Cu] = 4; 20 mm/min).

When the tensile tests are performed at 60 °C (Figure 11), only the sample with MW_{LPEI} 1115 retains tensile properties and behaves as an elastomer. The sample with MW_{LPEI} 440 is a soft and ductile material and the sample with MW_{LPEI} 185 is too soft to be measured.

Conclusions

The physical properties of LPEI–PTHF–LPEI block copolymers are dramatically modified by addition of $CuCl_2$. The formation of LPEI–Cu complex leads to a physical network structure. The properties of the complexed block copolymers are determined by the relative block sizes and by the salt contents. Materials with a wide range of bulk properties can be obtained by changing the chain length of LPEI and the copper ion content. When the LPEI blocks have molecular weights of 1100, the complexed block copolymers behave as tough thermoplastic elastomers.

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References and Notes

(1) Macknight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(2) Broze, G.; Jérôme, R.; Teyssie, Ph. *J. Polym. Sci., Polym. Lett.* **1981**, *19*, 415.
(3) Broze, G.; Jérôme, R.; Teyssie, Ph. *Macromolecules* **1981**, *14*, 224.
(4) Mohajer, Y.; Tyagi, D.; Wikes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Bull.* **1982**, *8*, 47.
(5) Desjardins, A.; Eisenberg, A. *Macromolecules* **1991**, *24*, 5779.
(6) Lu, X.; Weiss, R. A. *Macromolecules* **1993**, *26*, 3615.
(7) Zhou, Z.; Peiffer, D. G.; Chu, B. *Macromolecules* **1994**, *27*, 1428.
(8) Kaneko, M.; Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 397.
(9) Ciardelli, F.; Tsuchida, E.; Wöhrle, D. *Macromolecule-Metal Complexes*; Springer: Berlin, 1995.
(10) Eisenbach, C. D.; Göldel, A.; Terskan-Reinold, M.; Schubert, U. S. *Kautschuk Gummi Kunststoffe* **1998**, *51* (6), 422.
(11) De Witte, I. C.; Goethals, E. J. *Polym. Adv. Technol.* **1999**, *10*, 1.
(12) Saegusa, T.; Kobayashi, S. In *Polymeric Amines and Ammonium Salt*; Goethals, E. J., Ed.; Pergamon Press: Oxford, 1980; p 55.
(13) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*; John Wiley & Sons: New York, 1987; p 467.
(14) Kobayashi, S.; Hiroishi, K.; Tokunoh, M.; Saegusa, T. *Macromolecules* **1987**, *20*, 1496.
(15) D'Haese, F.; Goethals, E. J. *Brit. Polym. J.* **1988**, *20*, 103.
(16) Van Caeter, P.; Goethals, E. J.; Gancheva, V.; Velichkova, R. *Polym. Bull.* **1997**, *39*, 589.
(17) Dreyfuss, P. *Poly(tetrahydrofuran)*; Gordon and Breach, Science Publishers: New York, 1982; p 159.

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