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Gelation Behavior of Thermo-Responsive Poly(ethylene oxide) and Poly(propylene oxide) Multiblock Polycarbonates

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Multiblock polycarbonates were facilely synthesized by covalently binding poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks, using triphosgene as coupling agent. The resulting multiblock polycarbonates exhibited thermo-responsive gelation behavior. A pronounced viscosity increase was observed when the temperature increased, which was traced to the formation of a network of micelles. With further heating, the viscosity began to drop, which reflected breaking down of the network. Viscoelastic properties of the multiblock polycarbonates in aqueous solutions were probed by dynamic oscillatory techniques. At low frequencies, the systems showed a typical liquid-like behavior and at high frequencies they behaved as elastic materials. Data also showed that the network formed by polycarbonates with less EO/PO composition ratio evolved and strengthened, thus exhibited more elastic behavior. Temperature sweep results revealed that the aqueous solutions of polycarbonates underwent a sol-gel-sol transition with increasing temperature. By properly regulating the EO/PO composition, gelation occurred upon increasing the temperature to 37°C, which made it a promising candidate for an injectable drug delivery system.

Keywords: Gelation behavior, multiblock polycarbonates, thermo-responsive properties, poly(ethylene oxide), poly(propylene oxide)

1 Introduction

Thermo-responsive amphiphilic copolymers have been regarded as highly attractive materials due to their wide use in biomedical application, such as drug delivery, tissue engineering and other biomedical devices (1, 2). In particular, polymers capable of showing a sol-to-gel transition by temperature change constitute an active area of biomaterial research. The basic feature shared by thermo-responsive copolymers is that water solutions of these polymeric systems display low viscosity at room temperature, and exhibit a sharp viscosity increase as temperature rises within a very narrow temperature interval, producing a gel at body temperature (3, 4).The sol to gel transition of these polymers at low temperature can be utilized in the drug delivery applications since the transition temperature is around the body temperature (5–8). When the solution is exposed to the body by subcutaneous or intramuscular injection, it forms a gel *in situ*, entrapping the drug. The drug is then released by diffusion and-or by gel erosion from the surface which occurs upon dilution (9).

A number of thermo-responsive copolymers have been studied during the last decades, with much work focusing on poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO, Pluronics) triblocks. These triblocks have been widely used in various industries (10, 11) and their gelation mechanism is relatively well understood by many previous studies (12). For Pluronic F127 ($EO_{99}PO_{67}EO_{99}$), by adjusting the concentration of the polymer, the unimer-micelle equilibrium shifts towards to micellar state. When the aggregation number reaches the plateau value, the micelles come into contact with one another with increasing temperature. These contacts ultimately cause entanglements among the hydrophilic corona PEO chains, and finally, a gel structure is formed (13). However, these triblock materials are non-biodegradable and their gel phases are found to dissolve in vivo in short time upon dilution (14). Therefore, the biodegradable copolymers composed of poly(ethylene glycol) (PEG) and biodegradable polyester, such as poly(L-lactic acid) (PLLA), poly(D,L-lactic acid) (PDLA), poly(lactic acid-co-glycolic acid) (PLGA) and poly(D,L-lactic acid-co-caprolactone) (PDLA-co-PCL), have been investigated extensively during the past years. (15–19). *In situ* gel formation makes these copolymers solutions promising injectable biomaterials. Regrettably, in most of the studies, the sol-gel-sol transition temperatures were measured by a vial method which could introduce discrepancies in the

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determination of the solution-soft gel or soft gel-hard gel transitions (20). Instead, rheology can be regarded as a useful means to characterize sol-gel-sol transition (21, 22). In our study presented here, we synthesized a series of thermo-responsive multiblock polycarbonates consisting of PEO and PPO, and the sol-gel-sol transition of them was characterized by rheology. Furthermore, we not only presented the sol-gel-sol transition temperature, but also provided the detailed mechanism that governed the gelation properties of these systems.

Multiblock polycarbonates reported here were synthesized by coupling poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) through one-step condensation copolymerization, using triphosgene as coupling agent and pyridine as catalyst. This allows a new class of thermo-responsive copolymers to be made. The gelation behavior of the aqueous fluids was characterized in terms of steady-state shear measurements and dynamic oscillatory techniques. Based on these results, we suggested a gelation mechanism for the aqueous solutions of multiblock polycarbonates.

2 Experimental

2.1 Materials

Poly(ethylene glycol) (PEG) with a molecular weight of 6000 g/mol was supplied by Sinopharm Chemical Reagent Co., Ltd and purified by dissolving in dried chloroform followed by filtration and precipitation in anhydrous ethyl ether before use. Poly (propylene glycol) (PPG) with molecular weight of 2000 g/mol, purchased from Sinopharm Chemical Reagent Co., Ltd was dried at 120°C under vacuum for 2 h. Triphosgene was purchased from Yao and Shun Import and Export Co., Ltd and used without further purification.

2.2 Synthesis of the PEG/PPG Multiblock Polycarbonates

As a typical example, preparation of various PEG/PPG multiblock polycarbonates was described as follows. Briefly, PEG6000 (12.033 g, 2 mmol) and PPG2000 (4.008 g, 2 mmol) were dissolved in 30 mL of CH_2Cl_2 placed into a three-neck flask. 2.6 mL of anhydrous pyridine was poured as a catalyst and the mixture was cooled in an ice bath (0–5°C). A solution of triphosgene (1.826 g, 6 mmol) in 10 mL of $CH_2Cl_2$was added to this mixture dropwise during 90 min under magnetic stirring. After the dropping, the mixture was stirred for 45 min at room temperature. Then the polymerization was carried out at 40°C for 6 h with stirring. The resultant copolymer was precipitated from diethyl ether, and further purified by redissolving into methylene chloride followed by precipitation in a mixture of methanol and diethyl ether (4:1 in volume fraction). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS), δ (ppm): 3.35–3.85 (m, $-OC\mathit{H}_2-C\mathit{H}_2-$ and $-OC\mathit{H}(CH_3)-C\mathit{H}_2-$), 1.15–1.17 (d, $-OCH(C\mathit{H}_3)-CH_2-$), 4.25–4.30 (t, $-CH_2C\mathit{H}_2OCO-$), 4.85–4.90 (m, $-COOC\mathit{H}(CH_3)\ -CH_2-$), 1.25–1.30 (m, $-COOCH(C\mathit{H}_3)CH_2-$). IR (KBr, cm^{-1}): 1749 (C=O), 1264 (C–O), 754 (C–H).

2.3 Samples Preparation

A series of the multiblock polycarbonate aqueous solutions were prepared by slowly adding of predetermined amount of polycarbonates to cold distilled water followed by stirring. Then, the sample solutions were kept at 4°C for 24 h to equilibrate before the rheological measurements.

2.4 Characterization of the PEG/PPG Multiblock Polycarbonates

The ^{1}H-NMR spectrum was recorded in $CDCl_3$ solventon a Bruker AV-400 NMR spectrometer at 400 MHz with tetramethylsilane (TMS) as an inert standard at room temperature.

Gel permeation chromatography (GPC) measurements were carried out in DMF (1 mL/min) at 40°C using a Waters 515 liquid chromatography equipped with three styragel columns and a refractive index detector.

Rheological properties were studied using a HAAKE RS75 Rheometer. A cone-and-plate (C20/1*Ti, cone diameter and angle are 35 mm and 2°) fixture was used to carry out the measurements. The rheological behavior of our samples was determined under both steady and oscillatory shear to obtain the steady shear viscosity and dynamic viscoelastic properties of the polycarbonate solutions. Each sample was equilibrated for 10 min before starting the rheological analyses to eliminate the mechanical history.

2.4.1. *Viscometry test*

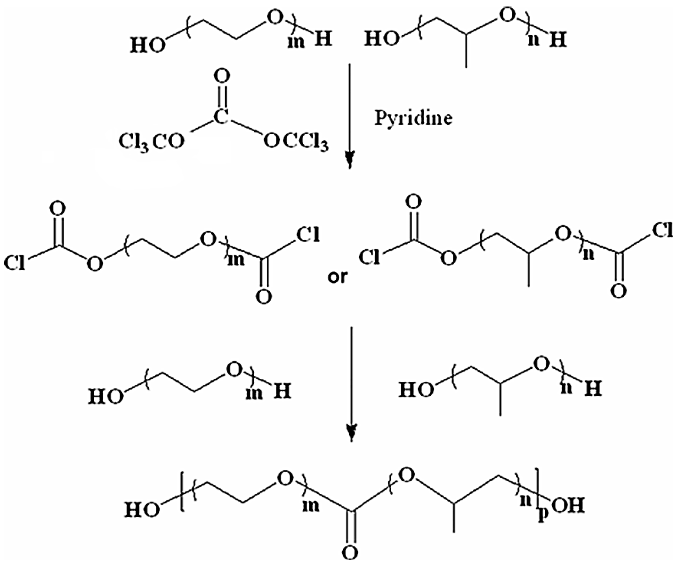
The temperature-dependent behavior of the polycarbonates system was studied in the temperature range of 15–70°C at the shear rate of 10 s^{-1}. The heating rate was 0.8°C/min.

2.4.2. *Oscillation stress sweep*

In oscillatory measurements, the rheological parameters were measured as a function of stress at a frequency of 1 Hz in 50 steps to obtain the linear viscoelastic region. The temperature was controlled at 25°C. Once the linear region was obtained, the rheological measurements were made as a function of frequency at a fixed stress.

2.4.3. *Frequency sweep*

After a proper stress of 85 Pa was selected, frequency sweeps were performed with the frequencies varying from 0.01 to 25 Hz at 25°C. The frequencies and the modulus values were then plotted in logarithmic scale.



Sch. 1. Synthesis of PEG6000–PPG2000 multiblock polycarbonates.

2.4.4. *Temperature sweep*

The sol-gel-sol transition temperature was determined by oscillation temperature sweep at a frequency of 1 Hz. The shear stress was kept constant at 20 Pa, which was in the linear viscoelastic region. The temperature range was 25–70°C and heating rate was 0.8°C/min. Mineral oil was added to the edge of the cone to prevent the dehydration during the rheological experiments.

3 Results and Discussion

3.1 Multiblock Polycarbonates Synthesis

Thermo-responsive PEG/PPG multiblock polycarbonates were synthesized by covalently coupling PEG and PPG, using triphosgene as coupling agent and pyridine as catalyst. The reaction process was shown in Scheme 1. The molecular weight of PEG and PPG were fixed at 6000 g/mol and 2000 g/mol, respectively. Three multiblock polycarbonates with initial PEG/PPG feed molar ratios of 0.8/1, 0.9/1 and 1/1 were synthesized and were coded as EO-CO-PO-0.8, EO-CO-PO-0.9 and EO-CO-PO-1. The structures of the polycarbonates were confirmed by ^{1}H NMR and the molecular weight and polydispersity of the polycarbonates were determined by GPC as summarized in Table 1. The feed molar ratios of PEG/PPG were 0.8/1, 0.9/1 and 1/1, thus the corresponding EO/PO molar ratios were 3.2/1, 3.6/1 and 4/1, respectively. However, the actual EO/PO molar ratio in copolymers (shown in Table 1) obtained from ^{1}H-NMR deviated from the designed values, which was probably attributed to the incomplete copolymerization and the removal of oligomers during the purification process. The polymerization yields ranged from about 50 to 66% after isolation and purification as shown in Table 1. All GPC traces of the multiblock polycarbonates were unimodal and showed low polydispersity, indicating that the purity was enough for the study of rheological properties of these multiblock copolymers.

3.2 Viscosity Vs. Temperature Profiles of the Polycarbonates Systems

Figure 1 presents the temperature-dependent behavior of the apparent viscosity for 15 wt% polycarbonates systems with varied composition. As it is clearly shown in the plots, all of the three polycarbonates exhibit thermo-responsive properties. A sharp increase in viscosity can be observed in the plots for each sample, and then the viscosity drops dramatically with the elevated temperature for EO-CO-PO-0.8 and EO-CO-PO-0.9. Taking EO-CO-PO-0.8 for example, when it is heated, an abrupt change in viscosity is observed and a plateau viscosity exists in the temperature range between 30°C and 42°C. This can be traced to the formation of a network of micelles which is broken by the shear flow, as previously reported by Bromberg on the star-branched PEO-PPO-PEO networks (23). With further heating, the viscosity begins to drop, which reflects the breaking down of network. The viscosity lowers till the temperature reaches around 60°C. As for EO-CO-PO-1, only the increase process of the viscosity is observed as shown in the insert of Figure 1, no viscosity decrease is observed up to 66°C (temperature was not elevated beyond 70°C due to the risk of water evaporation despite the use of a solvent trap). The sharpness of the plots and the magnitude of viscosity values decrease with increasing EO/PO composition of the

Table 1. Molecular characteristic of PEG6000-PPG2000 multiblock polycarbonates

Sample	*PEG/PPG (feed mole ratio)*	*EO/PO*[a]	M_n^b	M_w^b	M_w/M_n^b	*Yield/% (after purification)*
EO-CO-PO-0.8	0.8/1	4.4/1	98000	138000	1.41	51.82
EO-CO-PO-0.9	0.9/1	5.2/1	101000	123000	1.22	65.9
EO-CO-PO-1	1/1	6.8/1	99000	127000	1.28	49.7

[a] Obtained from ^{1}H-NMR measurements.
[b] Obtained from GPC measurements.

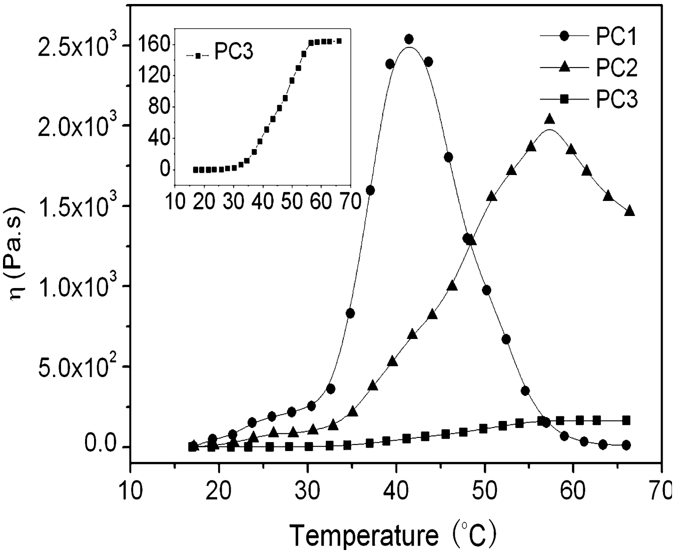


Fig. 1. The effect of temperature on the flow curves of 15 wt% aqueous solutions of EO-CO-PO-0.8 (PC1), EO-CO-PO-0.9 (PC2) and EO-CO-PO-1 (PC3).

polycarbonates. This suggests that the thermo-responsive behavior is dependent on EO/PO composition.

3.3 Viscoelastic Behavior of the Polycarbonates Systems

In oscillatory measurements, the rheological parameters were measured as a function of stress at a fixed frequency of 1 Hz to obtain the linear viscoelastic region in which storage modulus G' and loss modulus G'' are independent of the applied stress at any given frequency. Figure 2 depicts the stress sweep results for 20 wt% aqueous solutions of multiblock copolymers EO-CO-PO-0.8, EO-CO-PO-0.9 and EO-CO-PO-1 at 25°C, more impressive results can be easily grasped. For EO-CO-PO-1 (Figure 2a), the values of G' and G'' are considerably smaller compared with that for EO-CO-PO-0.8 and EO-CO-PO-0.9. Furthermore, G' is smaller than G'' andG' exhibits great fluctuation in the frequency range measured, which reveals that the viscous component maintains dominating in 20 wt% aqueous solution of EO-CO-PO-1. However, for EO-CO-PO-0.8 and EO-CO-PO-0.9, G' and G'' remain virtually constant with increasing stress up to the critical stress (σ_c) values of about 300 Pa, after that, G' and G'' begin to decrease whereas G' drops noticeably with further increase in the applied stress. At the same time, G' is always higher than G'', indicating that the elastic component is a larger proportion of the solution compared to its viscous component (24). Interestingly, G' andG'' values of EO-CO-PO-0.8 are larger than that of EO-CO-PO-0.9 as expected. For example, the storage modulus G' of EO-CO-PO-0.8 keeps fixed at about 100 Pa, while that of EO-CO-PO-0.9 is about 50 Pa. The values of G'' for EO-CO-PO-0.8 are

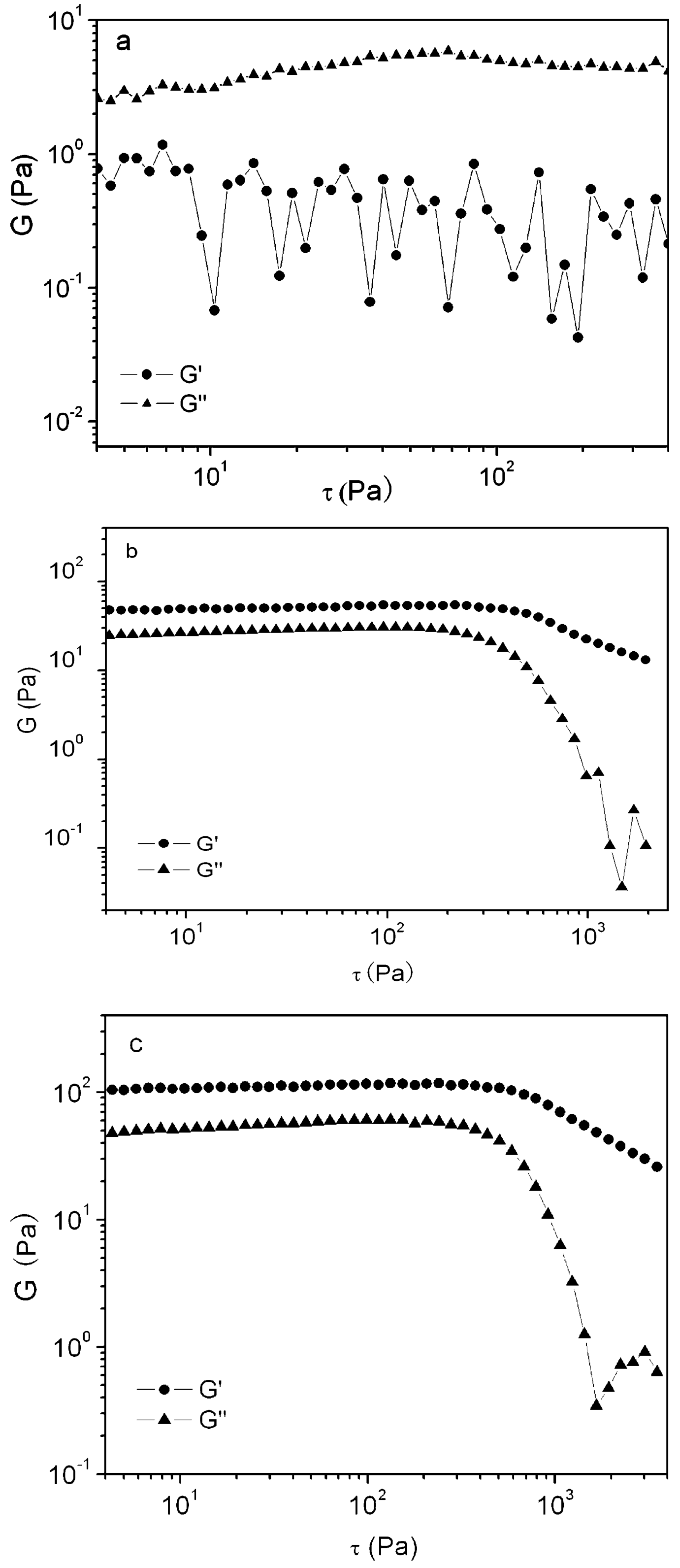


Fig. 2. Stress sweep results for 20 wt% aqueous solutions of (a) EO-CO-PO-1, (b) EO-CO-PO-0.9 and (c) EO-CO-PO-0.8 at 25°C.

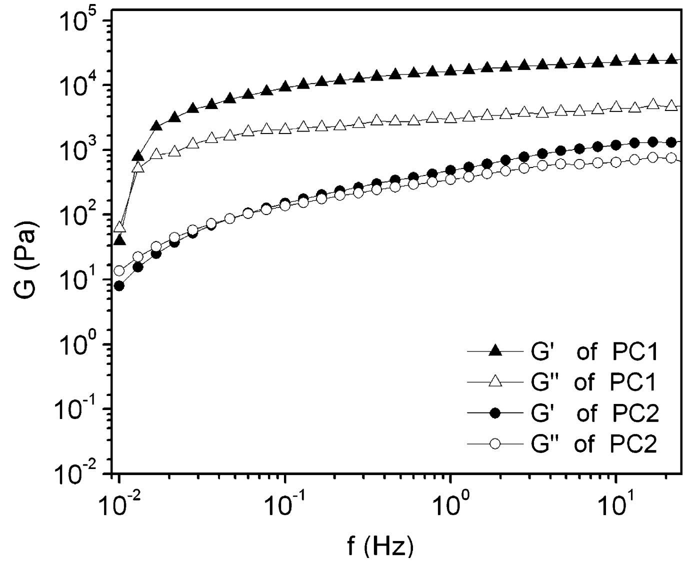


Fig. 3. Frequency sweep results for 20 wt% aqueous solutions of EO-CO-PO-0.8 (PC2) and EO-CO-PO-0.9 (PC1) at 25°C.

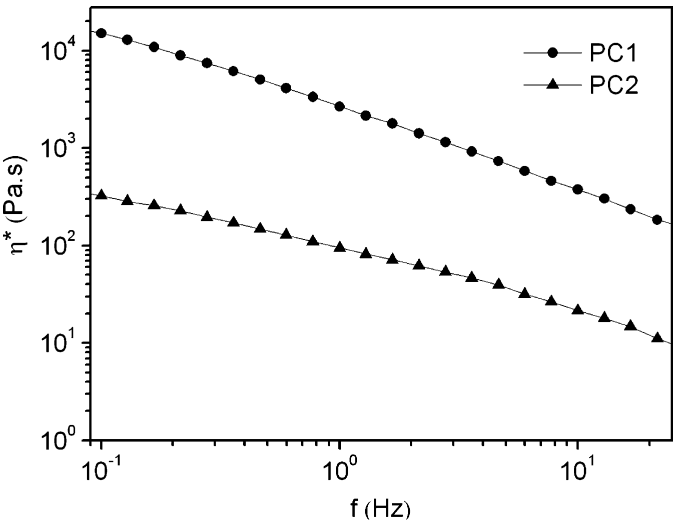


Fig. 4. Variation of complex viscosity as a function of frequency for 20 wt% aqueous solutions of EO-CO-PO-0.8 (PC1) and EO-CO-PO-0.9 (PC2) at 25°C.

almost two times as that for EO-CO-PO-0.9 at the plateau stage.

After a stress of 85 Pa was selected, the storage and loss modulus were measured to further compare the aqueous solutions properties of the polymers with different EO/PO composition ratios. Since EO-CO-PO-1 does not exhibit linear viscoelastic behavior, we show the results of the other two typical samples. As indicated by the frequency sweep curves in Figure 3, at low frequencies, the systems show a typically liquid-like behavior with $G'' > G'$. When it is shifted to high frequencies, a crossover from viscous to elastic behavior is observed with $G' = G''$. At still higher frequencies, the systems behave as an elastic material with $G' > G''$ and then G' tends to a plateau. These results suggest that the multiblock polycarbonate systems become more elastic at higher frequencies, which is typical for networks containing entangled or interconnected chains. Analogous phenomena were observed from Pluronic F68 ($EO_{78}PO_{30}EO_{78}$) system (25). What's more, when compared EO-CO-PO-0.8 with EO-CO-PO-0.9, the values of G' and G'' become larger over the applied frequency range. And the frequency of intersection ($G' = G''$) ω_c, shifts towards lower value, that is to say, the relaxation time λ ($\lambda = 1/\omega_c$) shifts towards longer time, indicating that the network formed by polycarbonates with less EO/PO composition ratio evolves and strengthens, thus exhibits more elastic behavior. From the oscillation experiments, frequency-dependent behavior of complex viscosity η^* was also obtained as shown in Figure 4, it can be observed that η^* decreases gradually at corresponding frequency range.

To make further analysis of the dynamic viscoelastic of the polycarbonate systems, we also measured a variation of G' and G'' with different aging time for 20 wt% aqueous solution of EO-CO-PO-0.8 that was incubated at body temperature. The results are presented in Figure 5. It can be seen that both G' and G'' decrease continuously with increasing aging time. After stored at 37°C for 5 days, the maximum values of G' decreases from around 25000 Pa initially to about 1300 Pa, while that of G'' slightly decreases from 5000 Pa to 1200 Pa. After 7 days, the sample turns to a viscous liquid as G'' become always higher than G'. The decrease of modulus has been proposed as an indicator of degradation of hydrogel, as previously reported in the case of PEG polymers (20). The change of η^* at corresponding frequency as shown in Figure 6 further validates these results.

The gelation behavior of the obtained polycarbonates was investigated by a temperature sweep method.

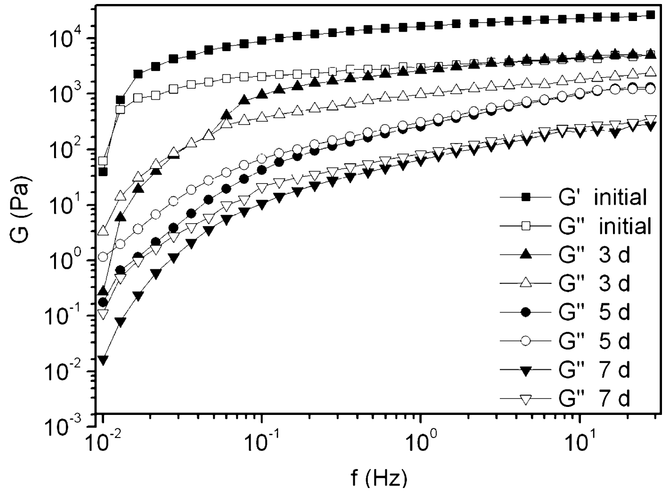


Fig. 5. Frequency sweep results for 20 wt% aqueous solution of EO-CO-PO-0.8 with different aging time at 37°C.

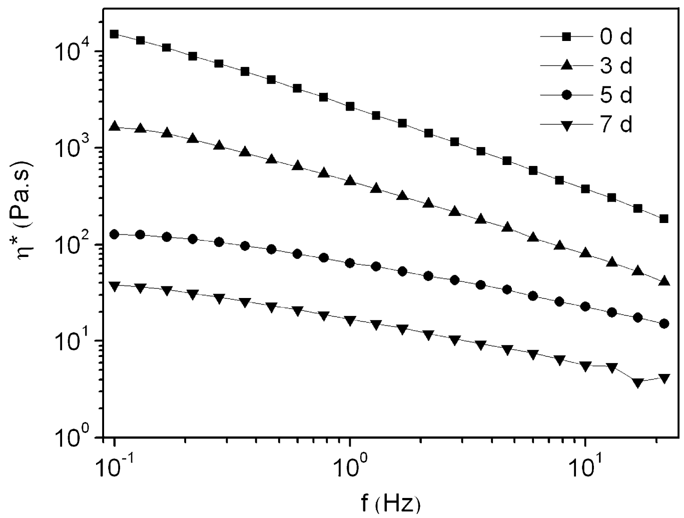


Fig. 6. Variation of complex viscosity as a function of frequency for 20 wt% aqueous solutions of EO-CO-PO-0.8 with different aging time at 37°C

Measurements of G' and G'' at a constant frequency (1 Hz) as a function of temperature for 15 wt% aqueous solutions of EO-CO-PO-0.9 are shown in Figure 7. At low temperature, the sample is in a liquid state with $G'' > G'$ as shown in inset A of Figure 7. As the temperature monotonically increases, an abrupt increase in G' is observed, which marks the onset of the gelation process. As soon as the temperature reaches about 37°C, a crossover of G' and G'' occurred, indicating that the samples underwent a sol-gel transition, forming an elastic network (26, 27). When checked, the stiff gel is found to be immobile over long time (shown in inset B of Figure 7). Then, G' and G'' continue increasing together until they get to the maximum values. The maximum G' obviously corresponds to the most compact micelle structure. The gel reverts back to a solution when the temperature is elevated to 56°C or even higher values (shown in inset C of Figure 7). Apparently, the gelatin physical network is broke down. Concomitantly, the complex viscosity η^* also exhibits abrupt increase and then pronounced decrease as temperature is elevated. It is of great importance to note that the sol-gel transition temperature for 15 wt% polycarbonate aqueous solution is 37°C, the presence of the gel phase at body temperature (37°C) suggests that the polycarbonates is a promising candidate for an injectable drug delivery system that can be prepared at room temperature and would form a gel *in situ* upon subcutaneous or intramuscular injection.

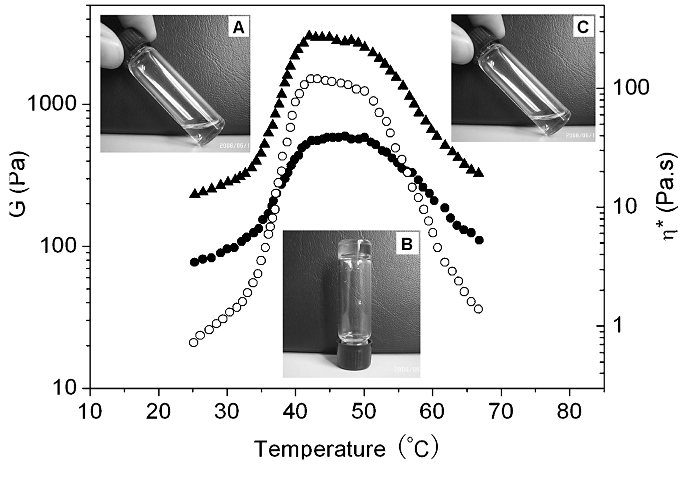


Fig. 7. Variation of storage modulus (open circles), loss modulus (solid circles) and complex viscosity (solid triangles) as a function of temperature for 15 wt% aqueous solutions of EO-CO-PO-0.9 and corresponding images in solution and gel states.

The gelation behavior observed from our PEG/PPG multiblock copolymers system appears different from those of EO and PO containing Pluronics system (P94, $EO_{21}PO_{47}EO_{21}$ and P103, $EO_{17}PO_{60}EO_{17}$) that show two gel states (28, 29), since the second gel state could not be detected from our systems. The reason for this distinction can probably be traced to the different composition between the two different systems. As explained by Park and co-workers (13), the first gelation was caused by the close packing of the micelles as the micelles became dominant over unimers and the micelle equilibrium was further shifted toward the micelles; the second gelation at high temperature was induced by more favorable hydrophobic attraction between the core PPO block phases. Because of the relatively low PPO composition of our polycarbonates compared to that of P94 or P103, it is not difficult to understand the absence of the second gel state for our system. It is also reasonable to think the relatively long PEO blocks somewhat suppress the entropy driven hydrophobic attraction by providing steric layers, thus only the sol-to-gel and gel-to-sol transitions are detected (30).

The gelation processes of EO-CO-PO-0.8 and EO-CO-PO-0.9 are further demonstrated in Figure 8 where the loss tangent, $\tan\delta = G''/G'$, is shown as a function of temperature ranging from 25°C to 70°C. For each polycarbonate, two stages along the temperature coordinate during the gelation process can be identified. An initial drop of tan δ occurs attributed to the initial rapid growth of clusters, which causes G' to become measurable (31). Next, G' and G'' increase together, until a gel network, composed of interconnected micelle is formed (25, 32). At higher temperatures, tan δ drops continually until it reaches minimum values at the temperature of about 40°C for EO-CO-PO-0.8 and 45°C for EO-CO-PO-0.9, indicating that the gel becomes much stiffer. At still higher temperature, tan δ shows a significant decrease, till a sol to gel transition emerges.

We also investigated the variation of complex modulus $G^*$and the dynamic viscosity η' over the temperature range 25–70°C at a fixed frequency of 1 Hz, where η' can be estimated as $\eta' = G'' / \omega$. The results for EO-CO-PO-0.8 and EO-CO-PO-0.9 are presented in Figure 9. First of all, both $G^*$and η' show a pronounced rise. This implies the degree

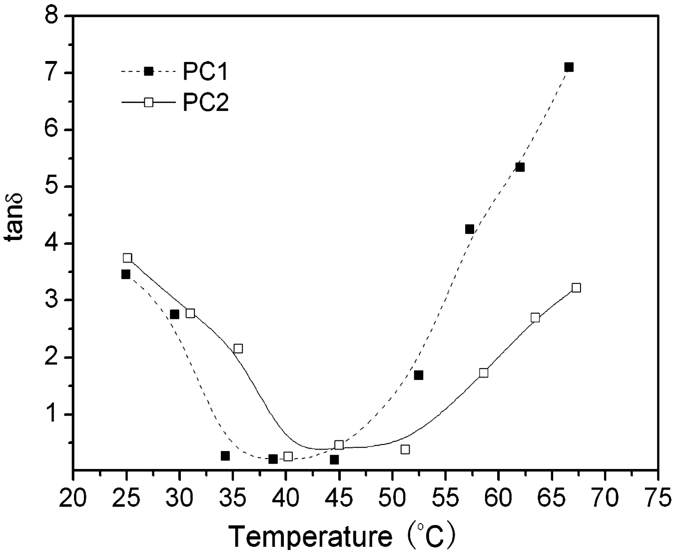


Fig. 8. Variation of loss tangent as a function of temperature for 15 wt% aqueous solutions of EO-CO-PO-0.8 (PC1) and EO-CO-PO-0.9 (PC2).

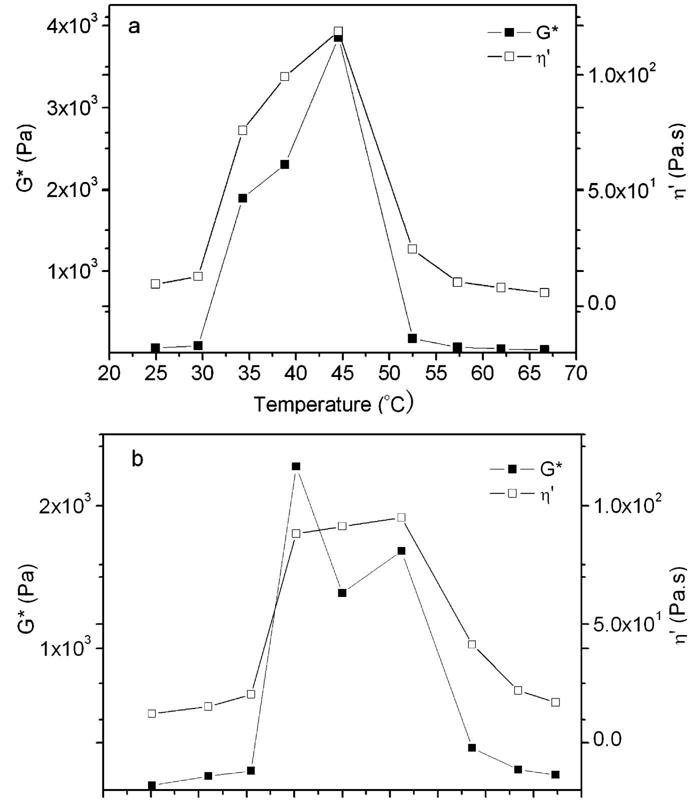


Fig. 9. Variation of complex modulus and dynamic viscosity as a function of temperature for 15 wt% aqueous solutions of (a) EO-CO-PO-0.8 and (b) EO-CO-PO-0.9.

Table 2. Sol-gel-sol transition temperature and corresponding transition modulus of multiblock polycarbonates aqueous solutions

Sample	*EO-CO-PO-0.8*				*EO-CO-PO-0.9*			
concentration/wt%	9	15	18	20	15	18	20	23
$T_{\mathrm{sol-gel}}$(°C)	42	32	26	17	37	31	26	19
$T_{\mathrm{gel-sol}}$ (°C)	48	51	55	63	56	61	68	—
$G_{\mathrm{sol-gel}}$ (Pa)	252	168	132	107	213	197	149	113
$G_{\mathrm{gel-sol}}$ (Pa)	393	215	187	167	351	269	273	—

of micellar packing changes with the increase in temperature (33), thus leads to the increase of the viscoelastic response for the system. With further heating, a decrease is observed, suggesting that the network formed by bridging between the micelles begins to break down (25). The temperature-depending behavior of $G^*$and η' for EO-CO-PO-0.8 (Figure 9a) resembles to that for EO-CO-PO-0.9 (Figure 9b), although there is a slight drop of G^* for EO-CO-PO-0.9 at the temperature of 45°C.

The sol-gel-sol transition temperatures as well as corresponding transition moduli of water-soluble EO-CO-PO-0.8 and EO-CO-PO-0.9 at different concentration were studied more detailed under the same conditions. The results are summarized in Table 2. For EO-CO-PO-0.8, hydrogels can be obtained with concentration higher than 9 wt%. The sol-gel transition temperature decreases from 42°C to 17°C when the concentration increases from 9 wt% to 20 wt%, whereas the corresponding transition modulus decreases from 252 Pa to 107 Pa. In contrast, the gel-sol transition temperature increases from 48°C to 63°C with the increasing concentration, concomitantly, the transition modulus decreases from 393 Pa to 167 Pa. When it comes to EO-CO-PO-0.9 with more PEO content, the gel phase is facilely demonstrated when its concentration is higher than 15 wt% and almost similar trends in the transition temperature and transition modulus are observed. The gel-sol transition is not observed when it at 23 wt% in the temperature range we measured. Therefore, hydrogels with different sol-gel-sol transition temperature and mechanical properties can be obtained by regulating the EO/PO composition ratio and the polycarbonate concentration.

4 Conclusions

Multiblock polycarbonates consisting of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) were synthesized using triphosgene as coupling agent and pyridine as catalyst. With increasing temperature, the polycarbonates exhibited a pronounced viscosity increase. This was caused by the quick packing of micelles, or the formation of physical gel network. The EO/PO composition ratios of the polycarbonates systems had a noticeable effect on the viscoelastic behavior of the systems. At low frequencies, the systems behaved like a viscoelastic liquid and at high frequencies like a viscoelastic solid. Rheological measurements also showed that a sol-gel–sol transition occurred with increasing temperature and by regulating the EO/PO composition ratio, the sol-gel transition could realize at 37°C, which made the systems suitable as an injectable drug delivery system.

Acknowledgements

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References

1. Hoffman, A.S. (2002) *Adv. Drug. Deliv. Rev.,* 54(1), 3–12.
2. Lee, K.Y. and Mooney, D.J. (2001) *Chem. Rev.,* 101(7), 1869–1880.
3. Sosnik, A. and Cohn, D. (2004) *Biomaterials*, 25(14), 2851–2858.
4. Sosnik, A. and Cohn, D. (2005) *Biomaterials*, 26(4), 349–357.
5. Jeong, B., Lee, D.S., Shon, J.I., Bae, Y.H. and Kim, S.W. (1999) *J. Polym. Sci. Part A: Polym. Chem.*, 37(6), 751–760.
6. Fults, K.A. and Johnston, T.P. (1990) *J. Parenter. Sci. Technol.*, 44(2), 58–65.
7. Johnston, T.P. and Miller, S.C. (1985) *J. Parenter. Sci. Technol.*, 39(2), 83–89.
8. Juhasz, J., Lenaerts, V., Raymond, P. and Ong, H. (1989) *Biomaterials*, 10(4), 265–268.
9. Johnston, T.P., Punjabi, M.A. and Froelich, C.J. (1992) *Pharm. Res.*, 9(3), 425–433.
10. Dong, J., Chowdhry, B.Z. and Leharne, S.A. (2005) *Colloids Surf. A*, 266(1–3), 191–199.
11. Dong, J., Chowdhry, B.Z. and Leharne, S.A. (2006) *Colloids Surf. A*, 277(1-3), 249–254.
12. Mortensen, K. and Pedersen, J.S. (1993) *Macromolecules*, 26(4), 805–812.
13. Park, M.J. and Char, K. (2002) *Macromol. Rapid Commun.*, 23(12), 688–692.
14. Jeong, B., Bae, Y.H. and Kim, S.W. (2000) *J. Biomed. Mater. Res.*, 50(2), 171–177.
15. Lee, J.W., Hua, F. and Lee, D.S. (2001) *J. Control. Release*, 73(2–3), 315–327.
16. Berglund, F. (1968) *Acta. Physiol. Scand.*, 73, 20A–21A.
17. Suh, H.R., Jeong, B.M., Rathi, R. and Kim, S.W. (1998) *J. Biomed. Mater. Res.*, 42(2), 331–338.
18. Jeong, B., Bae, Y.H., Lee, D.S. and Kim, S.W. (1997) *Nature*, 388(6645), 860–861.
19. Jeong, B., Bae, Y.H. and Kim, S.W. (1999) *Macromolecules*, 32, 7064–7069.
20. Li, F., Li, S., El Ghzaoui, A., Nouailhas, H. and Zhuo, R. (2007) *Langmuir*, 23(5), 2778–2783.
21. Li, H., Yu, G.E., Price, C., Booth, C., Hecht, E. and Hoffmann, H. (1997) *Macromolecules*, 30(5), 1347–1354.
22. Aamer, K.A., Sardinha, H., Bhatia, S.R. and Tew, G.N. (2004) *Biomaterials*, 25(6), 1087–1093.
23. Bromberg, L. (1998) *Polymer*, 39(23), 5663–5669.
24. Xin, X., Xu, G.Y., Wu, D., Li, Y.M. and Cao, X.R. (2007) *Colloids Surf. A*, 305(1–3), 138–144.
25. Nystroem, B. and Walderhaug, H. (1996) *J. Phys. Chem.*, 100(13), 5433–5439.
26. Vermonden, T., Besseling, N.A.M., van Steenbergen, M.J. and Hennink, W.E. (2006) *Langmuir*, 22(24), 10180–10184.
27. Li, F., Li, S. and Vert, M. (2005) *Macromol. Biosci.*, 5(11), 1125–1131.
28. Liu, Y., Chen, S.H. and Huang, J.S. (1998) *Macromolecules*, 31(7), 2236–2244.
29. Bahadur, P. and Pandya, K. (1992) *Langmuir*, 8(11), 2666–2670.
30. Kwon, K.W., Park, M.J., Bae, Y.H., Kim, H.D. and Char, K. (2002) *Polymer,* 43(11), 3353–3358.
31. Hodgson, D.F. adn Amis, E.J. (1990) *Macromolecules*, 23(9), 2512–2519.
32. Mortensen, K., Brown, W. and Joergensen, E. (1994) *Macromolecules*, 27(20), 5654–5666.
33. Park, M.J. and Char, K. (2004) *Langmuir*, 20(6), 2456–2465.