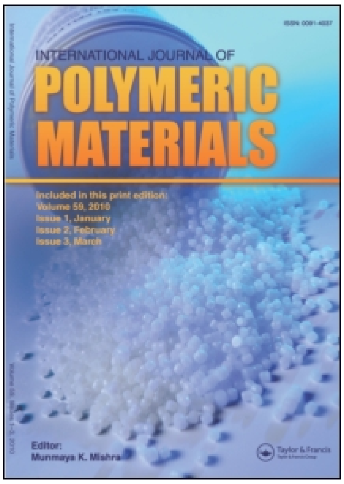

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# Rheological Behavior and Mechanical Properties of Blends of Poly(vinyl chloride) with CP-POSS

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# Rheological Behavior and Mechanical Properties of Blends of Poly(vinyl chloride) with CP-POSS

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In this work, a polyhedral oligomeric silsesquioxane which contains 3-chloropropyl groups (CP-POSS) was synthesized. The rheological behavior of CP-POSS/PVC blends was investigated by torque rheometer and capillary rheometer. Mechanical properties were investigated by electronic material tester. Influences of blending composition, shear rate and shear stress on melt apparent viscosity and non-Newtonian index (n) were discussed. The results show that the plastic time decreases and melt viscosity increases with increasing content of CP-POSS. CP-POSS has a good compatibility with PVC. The blend has the best impact strength when the content of CP-POSS is 7 wt%. The CP-POSS can be used as a processing aid and impact-resistant aid for PVC.

**Keywords** mechanical property, poly(vinyl chloride), rheology, silsesquioxane

## INTRODUCTION

Organic-inorganic hybrid nanocomposites have been regarded as a new generation of high-performance materials since they combine the advantages of both inorganic materials (rigidity, high stability) and organic polymers (flexibility, dielectric, ductility and processability) [1,2]. Polyhedral oligomeric silsesquioxanes (POSS), with great potential in the synthesis

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of organic/inorganic hybridized materials, have attracted much attention in recent years. POSS are generally synthesized through the hydrolytic condensation of organotrialkoxysilanes, $RSi(OR')_3$ [3,4]. The typical $T_8$ POSS monomers possess the structure of cube-octomeric frameworks with eight organic corner groups (see Scheme 1). The diversity of the organic groups on silsesquioxane cage can provide ones with tremendous space for maneuver to control the microstructure of POSS-containing hybrids. The organic functions make the POSS nanostructure compatible with polymers or monomers. This has been shown to apply to a wide range of thermoplastic and thermoset systems [5–7]. It allowed the POSS to be used as a modifier or reinforcer of several polymeric materials in recent years.

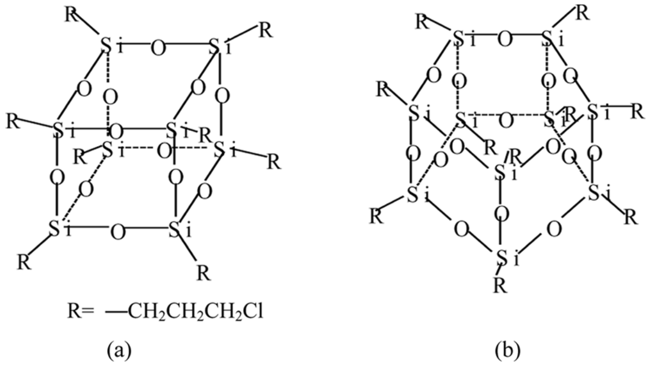
Poly(vinyl chloride) (PVC) is the third most consumed polymeric material worldwide, with wide applications in areas including construction, tubing, medical devices and electronics packaging [8]. But the pure PVC is a brittle material (i.e., a "hard" polymer) and does not have good processing behavior. The modification of PVC by adding another compound is a well-known method currently in practice. These modifiers may be divided into two basic groups: the first one involves rubberlike polymers (such as butadiene acrylonitrile rubber) or plasticity reagents, which can reduce the brittle nature or increase toughness. The other group is usually used as processing aids, which can improve the processing properties (milling, calendaring, extrusion, blow molding, and the like). The most commonly used plasticizers for PVC are phthalate esters (such as dioctyl phthalate, DOP, or dibutyl phthalate, DBP), and they are also good processing aids for PVC. But they all show adverse effects on glass transition temperature range, stiffness and strength. Furthermore, the conventional low molecular weight organic plasticizers are somewhat volatile, leading to plasticizer loss and unwanted deterioration of the material properties over the course of time.

In this article, a polyhedral oligomeric silsesquioxanes (CP-POSS), which contains 3-chloropropyl groups, was synthesized. The rheological behavior and mechanical properties of CP-POSS/PVC blends were investigated. Meanwhile, the glass transition temperature, $T_g$, of the blends was also determined by dynamic mechanical analyzer (DMA).

## EXPERIMENTAL

### Materials

Poly(vinyl chloride) was supplied by Yanshan Chemical Co., Beijing, China. The tribasic lead sulfate (TLS), dibasic lead phosphite (DLP), zinc stearate (ZS), wax, dibutyl phthalate (DBP) and tetramethylammonium hydroxide (TMAH), are all of commercial grade and were supplied by Beijing Chem. Co., China. 3-chlorine-propyltrimethoxysilane (CPTMS) was supplied by Shenda Chem. Co., Beijing, China.



**Scheme 1:** The structures of 3-chloropropyl-POSS $T_8$ and $T_{10}$ (a) $T_8$, and (b) $T_{10}$.

The polyhedral oligomeric silsesquioxane (CP-POSS) which contains 3-chloropropyl groups on silsesquioxane cage was synthesized by the hydrolytic reaction of CPTMS catalyzed with TMAH according to the literature [9,10]. The yield is 85 wt%. Liquid Chromatography—mass spectrometer (LC/MSD, 1100 type, Agilent, USA) was used for the determination of the components and the detailed structure of CP-POSS. The result shows that $T_8$ is the main product but contains a little $T_{10}$. The structures are shown in Scheme 1.

## Preparation of POSS/PVC Blend Samples

Six samples were prepared as following: 3 g tribasic lead sulfate (TLS), 2 g dibasic lead phosphite (DLP), 1.5 g zinc stearate (ZS), 0.5 g wax and 10 mL dibutyl phthalate (DBP) were added into 100 g PVC. Then 0 g, 3 g, 5 g, 7 g, 9 g and 11 g CP-POSS were added to the samples above, and marked as P0, P3, P5, P7, P9 and P11, respectively. All components were first mixed in a mixer and then milled on a laboratory two-roll mill at 160–180°C. A 5 mm thick plate was pressed at 170–180°C, then cold-pressed for 10 min at 5 Mpa to determine mechanical properties and rheological behavior.

## Determination of Plastic and Rheological Behavior

The plastic behavior of CP-POSS/PVC blends was investigated at 185°C using a torque rheometer (Ke Chuang XSS-300, Shanghai, China).

The rheological behavior of the blends was investigated by capillary rheometer (XLY-II, Jilin University, China). The fixed temperature method was used. The nozzle diameter is 1 mm and length is 20 mm. The weight of test specimen is 1.5 g.

## Determination of $T_g$

The $T_g$ of CP-POSS/PVC blends were investigated using a dynamic mechanical analyzer (DMA, DMA-8000, Perkin Elmer Co, USA). Sample size was $20 \times 5 \times 0.8$ mm. Heating rate was 2°C/min and the frequency is 2 Hz. The range of testing temperature was from −75 to 180°C.

## Determination of Mechanical Properties and Morphology

Tensile strength test was performed using an electronic tensile tester. Tests were conducted at an extension rate of 20.0 mm/min at 25°C and 50% relative humidity. The notch impact test was carried out on an XCJ-40 impact tester.

The morphological structure of the zone of fracture was investigated by scanning electron microscopy (SEM) [11].

# RESULTS AND DISCUSSION

## Plastic Behavior of CP-POSS/PVC Blends

Relationships between the balance torque, plastic time and the CP-POSS content are shown in Figure 1. As seen from Figure 1, the balance torque of blends increases with increasing content of CP-POSS; simultaneity, the plastic time decrease. This is because that CP-POSS has a lower viscosity, with an organic/inorganic hybridized structure. The 3-chloropropyl end group of POSS has a good compatibility with PVC molecules. CP-POSS has an ability

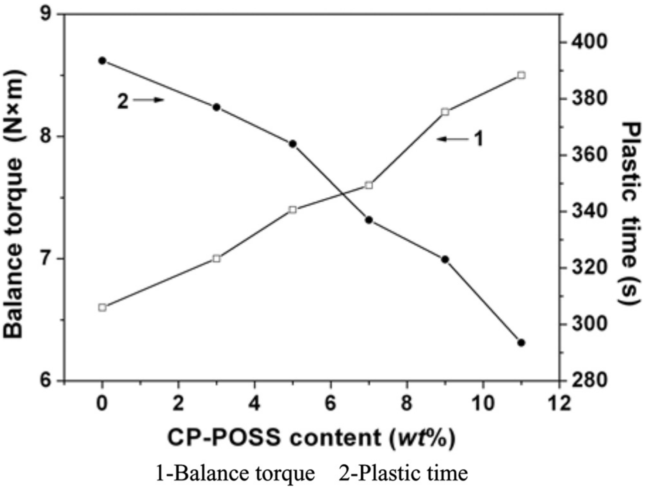


**Figure 1:** Relationship between the balance torque, plastic time and the CP-POSS content.

to plasticize PVC. In the mixture, the CP-POSS has a low melting point and the CP-POSS molecule, which is equivalent to nanometer particles, will fill into the free volume between PVC molecule chains. So the plastic time decreases with increasing content of CP-POSS. But the chlorine atom of 3-chloropropyl on POSS can form a weak hydrogen bond with PVC molecule. The hydrogen bonds hinder the movement of PVC chains. The friction force between PVC chains and CP-POSS increases, so the balance torque increases with the content of CP-POSS.

## Rheological Behavior of the CP-POSS/PVC Blends

The experimental temperature was fixed at 185°C, and experimental loads were 120, 160, 200, 240, 280, 320 and 360 $\mathrm{kg/cm^2}$. The apparent shear stress $\tau_w$, apparent shear rate $\dot{\gamma}_w$ and apparent viscosity $\eta_a$ were calculated using the following Equations [12]. Effective shear stress at the wall of nozzle is given by

$$\tau_w = \Delta PR/2L \tag{1}$$

where $\Delta P$ is the applied pressure ($\mathrm{kg/cm^2}$), $R$ is the nozzle radius (cm), $L$ is the nozzle length (cm).

The efflux rate is given by

$$Q = \frac{hs}{t}(\mathrm{cm^3/s}) \tag{2}$$

where $h$ is the downward displacement of plunger (cm), $s$ is the area of plunger ($\mathrm{cm^2}$), $t$ is the effluent time of melt (s).

Then the apparent shear rate at the wall of nozzle can be calclulated by

$$\dot{\gamma}_w = -\mathrm{d}\nu/\mathrm{d}r = 4\mathrm{Q}/(\pi \mathrm{R}^3) \tag{3}$$

According to Hagen-Poiseuille equation, the apparent viscosity was calclulated by

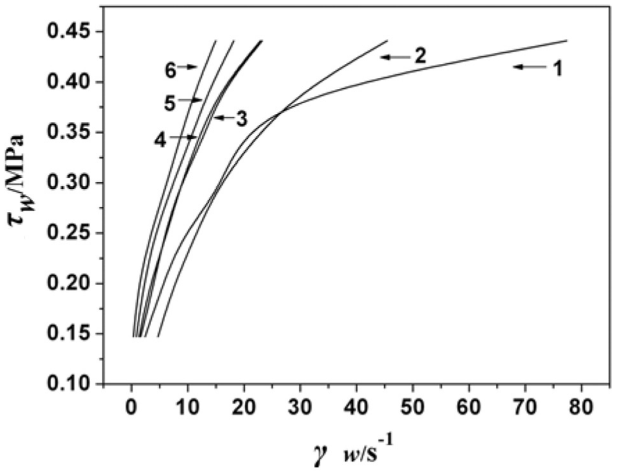
$$\eta_a = \pi \Delta PR^4/(8QL) \tag{4}$$

According to Ostwald-De Waele power-law Equation [12]:

$$\tau_\mathrm{w} = k\dot{\gamma}_w^n \tag{5}$$

where $k$ is constant, $n$ is the non-Newtonian parameter.

The plots of $\tau_w$ vs. $\dot{\gamma}_w$ are given in Figure 2. As seen from Figure 2, the apparent shear stress $\tau_w$ increases with increasing shear rates $\dot{\gamma}_w$. It is shown also that the sensitivity of $\dot{\gamma}_w$ to shear stress $\tau_w$ changes with different CP-POSS contents. When there is no CP-POSS added, the flow behavior of PVC in the melt is the behavior of shear thinning pseudoplastic liquid with



1-P0, 2-P3, 3-P5, 4-P7, 5-P9, 6-P11,

**Figure 2:** The relationship curves of $\tau_w$ with $\dot{\gamma}_w$ for CP-POSS/PVC blends.

increasing shear rate. The higher CP-POSS content, the bigger influence on $\tau_w$ to $\dot{\gamma}_w$; the character of pseudoplastic fluid decreases with an increase of CP-POSS.

The polymeric melt flow is a peristalsis process of macromolecular chain segments. A hard macromolecule usually has longer chain segments, and requires a long time to change from chain segment peristalsis to macromolecular centrobaric movement, so the melt will have a higher apparent viscosity. The CP-POSS is a molecule of multi-polar groups and has a large steric hindrance, which can increase the interaction between the PVC molecules and CP-POSS. Hence, it can form physical cross points (weak hydrogen bonds) between the chlorine atom of CP-POSS and the hydrogen atom of $-$CHCl$-$ on PVC molecular chains. These interactions slow the movement of molecular chain segments and the apparent viscosity of melt increases. The character of pseudoplastic fluid decreases with increasing content of CP-POSS. This result is coincident with the balance torque increases with increasing content of CP-POSS, as discussed above.

The non-Newtonian index $n$ can be obtained from the plot of ln $\tau_w$ vs. ln $\dot{\gamma}_w$ according Eq. (5). The result is shown in Figure 3. As seen from Figure 3, the $n$ values increase with the content of CP-POSS. It shows that the non-Newtonian property of melts decreases when CP-POSS is added. This is also because that the CP-POSS has a good compatibility with PVC and has larger interaction between CP-POSS molecules and PVC chains. The compatibility can be seen from Figure 4, since the mechanical loss spectra of CP-POSS/PVC blends which is obtained from test of DMA, are each only one sharp peak.

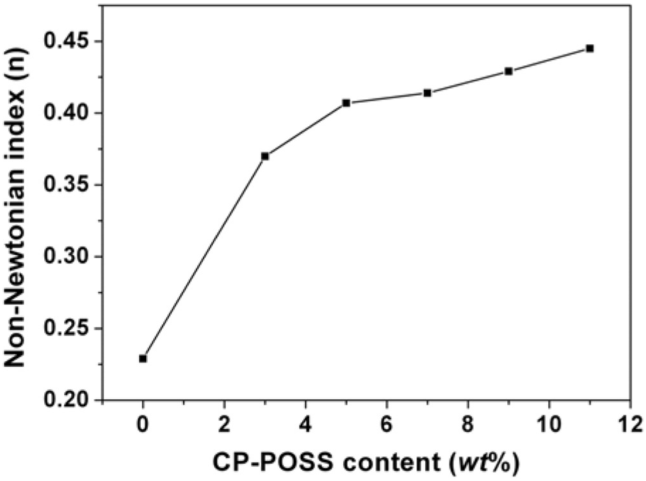
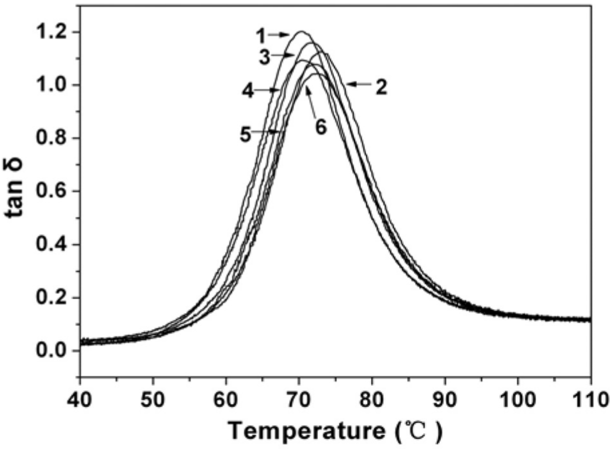


**Figure 3:** Relationship of *n* and CP-POSS content at 185°C.

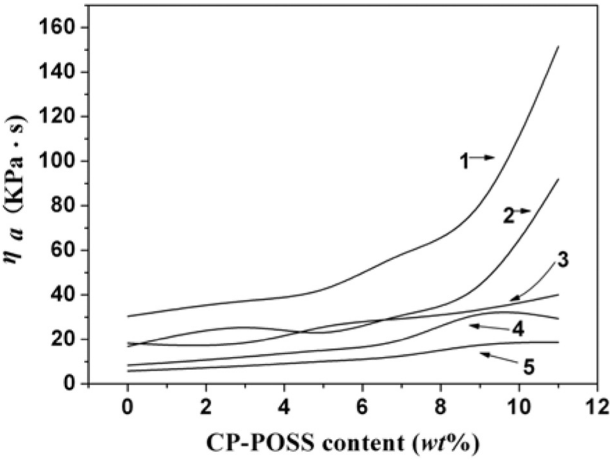
## Dependence of Melt Apparent Viscosity on CP-POSS Content

At a fixed shear stress of 34.3 MPa, the melt apparent viscosity $\eta_a$ of blends was investigated at 175, 180, 185, 190 and 195°C. As seen from Figure 5, the $\eta_a$ decreases with increasing temperature when the CP-POSS content is the same in the blends. When the experimental temperature is lower than 180°C, the melt viscosity will increase with increasing content of CP-POSS at the same temperature. This result is also coincident with the fact that



1-P0 2-P3 3-P5 4-P7 5-P9 6-P11

**Figure 4:** Relationship of tan $\delta$ and temperature.



1-175°C, 2-180 °C, 3-185 °C, 4-190 °C, 5-195 °C

**Figure 5:** Melt viscosities of blends at different temperature.

balance torque and non-Newtonian index $n$ increase with increasing content of CP-POSS. But when the experimental temperature is over 180°C, the increasing trend of melt viscosity with the CP-POSS content is decreased at that temperature. This is because that the hydrogen bonds and action force between molecules are function of temperature [13], the hydrogen bonds will break and action force between molecules will be weaken at higher temperature. The chain segment peristalsis at higher temperature is easier than it at lower temperature. So the influence of CP-POSS content on $\eta_a$ at higher temperature is weaker than at lower temperature.

## Dependence of $T_g$ on CP-POSS Content

Table 1 shows the $T_g$ data of CP-POSS/PVC blends which was obtained from DMA. As seen from Table 1, $T_g$ is enhanced when CP-POSS is added to PVC, but the value of $T_g$ increases only 2–3°C and the highest $T_g$ is at 73.3°C for P3 sample. The little increase of $T_g$ can be attributed to molecular interaction of PVC and CP-POSS. Multi-polar groups in CP-POSS molecule can form physical cross points with PVC molecules. But the CP-POSS has a

**Table 1:** $T_g$ of CP-POSS/PVC blends.

| **Sample No.** | **P0** | **P3** | **P5** | **P7** | **P9** | **P11** |
|---|---|---|---|---|---|---|
| CP-POSS content (wt%) | 0 | 3 | 5 | 7 | 9 | 11 |
| $T_g$ (°C) | 70.7 | 73.3 | 72.2 | 72 | 72.5 | 72.6 |

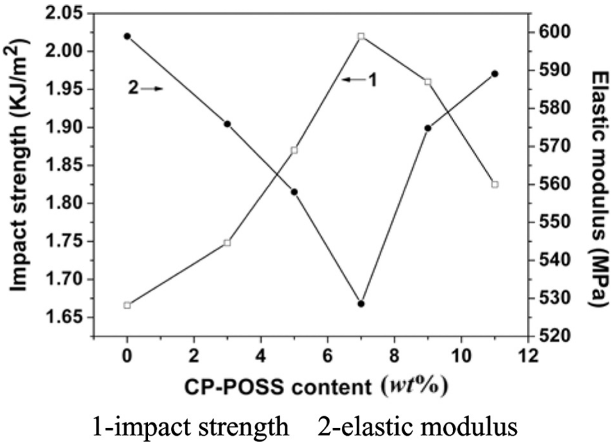


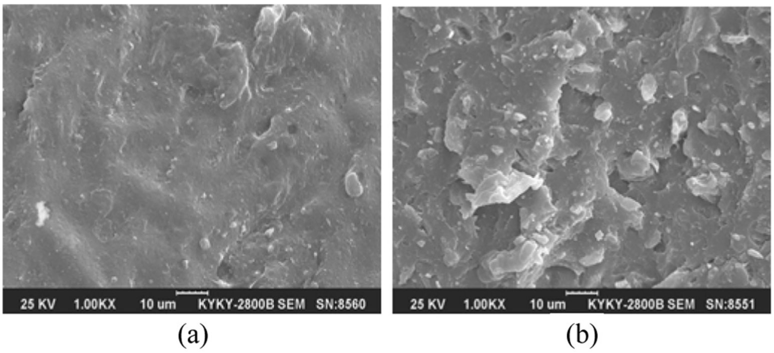
**Figure 6:** Relationship between impact strength, elastic modulus and CP-POSS content.

lower melting point and has a plasticzing action on PVC, so the $T_g$ increases only a little.

## Mechanical Properties

Figure 6 shows the data of impact and tension strength. As seen from Figure 6, the blends have better impact strength when the CP-POSS content is 3–11 wt%, and has a best value at 7 wt%, but the tension strength has a lowest value at 7 wt%. Therefore, the CP-POSS can increase the impact strength of pure PVC as a plasticity agent, but it also has some action to increase tension strength when the content is over 9 wt%.

Figure 7 shows the SEM photographs of the impact fractured surface of P0 and P7. As seen from Figure 7, the P0 (pure PVC) has a smooth fracture surface and exhibits a brittle break; it is the breaking character of brittle



(a)

(b)

**Figure 7:** SEM photographs of impact breaking surface of P0 and P7 (a) P0, and (b) P7.

material. The fracture behavior of P7 shows some toughness characteristics, its fracture surface is not smooth, and there are many holes, which is the breaking character of tough materials. These results are also consistent with the discussion about plastic action of CP-POSS in blends and physical cross links between PVC molecules and CP-POSS. When the CP-POSS content is lower than 7 wt%, the plasticization effect is the main effect, the impact strength increases. When the CP-POSS content is over than 9 wt%, the interaction between PVC molecules and CP-POSS has a larger effect on molecular movement, so that the impact strength decreases and tension strength increases.

## CONCLUSION

The 3-chloropropyl-POSS (CP-POSS) has a good compatibility with PVC and a plasticizing effect on PVC. It can decrease plastic time, but the melt viscosity increases because of the interaction between CP-POSS and PVC molecules. The CP-POSS can increase impact strength and has a best value when the content of CP-POSS is 7 wt%. But the impact strength decreases and tension strength increases when the content of CP-POSS is over 7 wt%. The CP-POSS can be used as a processing aid and impact-resistant aid for PVC.

## REFERENCES

[1] Agaskar, P. A. *Inorg. Chem.* **30**, 2707 (1991).

[2] Dell'Erba, I. E., and Williams, R. J. J. *European Polymer Journal* **43**, 2759 (2007).

[3] Kopesky, E. T., Mckinley, G. H., and Cohen, R. E. *Polymer* **47**, 299 (2006).

[4] Tsai, M. H., and Whang, W. T. *Polymer* **42**, 4197 (2001).

[5] Zhang, Z., Liang, G., Wang, J., and Ren, P. *Polym. Compos.* **28**, 175 (2007).

[6] Gao, J. G., Kong, D. J., and Li, S. R. *Intern. J. Polym. Mater.* **57**, 940 (2008).

[7] Joshi, M., and Butola, B. S. *Polymer* **45**, 4953 (2004).

[8] Rahman, M., and Brazel, C. S. P. *Polym. Sci.* **29** (48), 1223 (2004).

[9] Gao, J. G., Jiang, C. J., and Zhang, X. J. *Intern. J. Polym. Mater.* **56**, 65 (2007).

[10] Saito, H., and Isozaki, M. Japan, [31] **285387**[P], (2002).

[11] Yin, J. H., and Mo, Z. S. *Modern Polym. Phys.* **2**, 591 (2003).

[12] Gao, J. G., Li, D., Wang, D., and Yang, L. T. *Eur. Polym. J.* **36**, 2517 (2000).

[13] Dormidontova, E., and Brinke, G. *Macromolecules* **31**, 2649 (1998).