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Shear stress analysis of a semiconducting polymer based electrorheological fluid system

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Abstract

The electrorheological characteristics of a fluid system with semiconducting poly(naphthalene quinone) (PNQR) particles, synthesized from a Friedel–Craft acylation, were investigated via a rotational rheometer equipped with a high voltage generator. The flow curves of these ER fluids under several applied electric field strengths and particle concentrations were constructed and their flow characteristics were examined via three different rheological constitutive equations of Bingham model, De Kee–Turcotte model and our proposed model. Our proposed equation was found to fit the data very accurately.

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1. Introduction

Electrorheological (ER) fluids, which are suspensions of polarizable particles in a non-conducting liquid, exhibit drastic changes in rheological properties under an applied electric field. By tuning fibrillar structures with controlled electric field strength, microstructural transition from liquid-like to solid-like is obtained. Polarizable particles, under an external electric field, behave as electric dipoles, which attract each other to form chain and column structures aligned along the field direction [1]. Recently, it also has been realized that the conductivity mismatch between particles and fluid is a dominant factor in determining the ER characteristics, such as yield stress [2], especially at a high electric field strength. All physical and mechanical properties changes induced by the applied electric field are virtually instantaneous and are reversible upon the removal of the external field.

Despite numerous reports [3–11], further investigations are still required on rheological behaviors of the ER fluids. ER fluids exhibit non-linear response when exposed to external electric fields, and are generally considered as field-induced Bingham fluids. When the solid-like state of ER fluids, induced by an applied electric field, is forced beyond a certain amount of stress, the suspensions begin to flow. However, ER fluids do not always behave as typical Bingham fluids, which show either Newtonian or pseudo-plastic behavior after a yield point, since ER fluids exhibit a transition zone in a low shear-rate regime [12]. This phenomenon is related to the breakage rate of the chain structures caused by the applied shear and is related to the rate of structure reformation induced by an external electric field. A semiclassical theory was also proposed to describe the yield stress as a function of particle concentration based on the idea that the ER effect can be described via a coupling between phonon-like and polariton-like waves that propagate across the solid–liquid medium [13].

Various polymeric particles have been introduced, as a dispersed phase, to avoid the thermal breaking, particle settling, irreversible clumping, and abrasiveness. These polymeric particles are polyaniline [14,15] and its derivatives [16,17], poly(acene quinone) radicals (PAQRs) [18], poly(*p*-phenylene) [19], polyphenylenediamine [20], and polypyrrole [21], which are thermally stable and relatively easy to synthesize. Recently, polymer/inorganic nanocomposites [22–25], polythiophene [26], polyisoprene-*co*-poly(*tert*-butyl methacrylate) [27], microencapsulated polyaniline [28], and biopolymers [29,30] have also been investigated as candidate materials for dry-base ER fluids.

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PAQRs exhibit various electrical and physical properties depending on both monomer composition (acenes and anhydrides) and polymerization temperatures. These PAQR-based ER fluids have been used as an anhydrous ER system. Block et al. [18] used 1,2,4,5-benzenetetracarboxylic dianhydride, and Choi et al. [31] used phthalic anhydride for the polymerization of PAQRs. Several ER fluids in the PAQRs family including poly(naphthalene quinone) radicals (PNQR), poly(anthracene quinone) radicals, and poly(pyrene quinone) radicals were reported and the PNQR system demonstrated the best ER performance with the largest yield stress among its family [31].

In this work, the PNQR was synthesized and then used as particles for ER fluids. The rheological properties of these ER fluids including the yield stresses were measured at several applied electric field strengths by a rotational rheometer equipped with a high-voltage generator. Note that the shear stress of ER fluids in general has been investigated as a function of either applied electric field strength [32,33] or particle concentration.

2. Experimental

The PNQR was synthesized using naphthalene (Junei Chemical Co., Japan) and phthalic anhydride (Duksan Pure Chemical Co., Korea) as monomers, and zinc chloride (Duksan Pure Chemical Co., Korea) as a catalyst in a Friedel–Crafts acylation between naphthalene and phthalic anhydride. To achieve uniform polymer properties, polymerizations took place in an inert gas environment as described by Choi et al. [31]. The reaction temperature was maintained at 250 °C, and the polymerization was complete after 24 h (Fig. 1).

The synthesized polymer was ball-milled with a dilute, aqueous HCl solution to remove the catalyst and to control the particle size. After milling, the mixture was filtered with a 38 sieve. The particles were then purified by an extraction process sequentially using water, ethanol, and benzene in a Soxhlet apparatus to remove any unreacted monomer and oligomers. Finally, the polymer particles were dried in a vacuum oven.

The conductivity of the PNQR was measured to be $3.33\times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ using a 2-probe method with a pressed disk of polymer having silver electrodes on each side. In contrast to the commonly used semiconducting polyaniline-based ER materials in which the conductivity of the synthesized polyaniline is controlled by a doping and dedoping process, the desired conductivity of the PNQR for an ER application was easily obtained. The density was obtained to be 1.69 g/ml using a pycnometer. In this paper, all measurements were taken at 25 °C unless specified. Choi et al. [31] employed the FT-IR spectra, thermo-gravimetric analysis, and density data for polymer characterization, since standard molecular characterization techniques, such as viscometry and light scattering techniques, cannot be used because PNQRs are insoluble and infusible in most solvents.

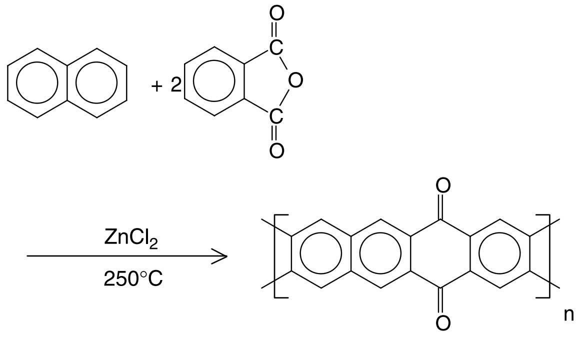

Fig. 1. The polymerization reaction for PNQR.

ER fluids consisting of silicone oil (Shin-Estu, Japan) and the PNQR polymer particles were prepared at three different volume fractions ($\phi = 0.05$, 0.15 and 0.25). The kinematic viscosity of the silicone oil was 30 cS, and its density was 0.955 g/ml. The silicone oil was dried in a vacuum oven and then stored in a bottle with a molecular sieve to remove any trace of moisture. Finally, the ER fluids were stored in a desiccator to prevent the adsorption of moisture.

A rotational rheometer (Physica MC120, Germany) equipped with a high voltage generator (HVG 5000, Germany) was used to determine the rheological properties of the ER fluids, using a concentric, cylinder-type (Z3-DIN: gap between bob and cup is 1.06 mm) measuring system. The HVG 5000 could supply a DC voltage up to 5 kV/mm within ±10 mA of electric current. During the test, an ER fluid was placed between the bob and cup of the rheometer, and a DC voltage was applied to the cup. The voltage was applied for 3 min to obtain equilibrium, chain-like (columnar) structures before applying shear.

Steady shear experiments were performed using both controlled shear stress and controlled shear rate (CSR) modes. Shear stress and viscosity, in a broad range of shear rates (0.005–1000 s^{-1}), were measured using the CSR mode.

3. Results and discussion

Fig. 2(a) and (b) show the ER behavior of shear stress (τ) and apparent shear viscosity (η) as a function of the shear rate ($\dot{\gamma}$) for 25 vol% of PNQR under four different electric field strengths (E) from the controlled shear rate mode. The shear rate is defined as $\dot{\gamma} = 2D_o^2\omega/(D_o^2 - D_i^2)$. Here ω is the angular velocity of the rotating cylinder, and D_o and D_i are the diameters of the outer and inner cylinder [34], respectively. The shear stress (or shear viscosity) increased drastically under the applied electric field strength as compared to the zero electric field strength case, although the shear viscosity decreased with shear rate.

Furthermore, Fig. 2(a) shows a shear stress plateau for a broad range of shear rates under an applied electric field. This represents a yield behavior in which particle chain structures, induced by electric field, break down via deformation. Due to the same reason, η decreases via a power law in $\dot{\gamma}$ ($\eta = \dot{\gamma}^{-n}$) as shown in Fig. 2(b). This shear thinning behavior is another characteristic feature of ER fluids. In the stress plateau, electrostatic interactions within particles due to an applied electric field and hydrodynamic interaction caused by external shear flow compete with each other, and electrostatic

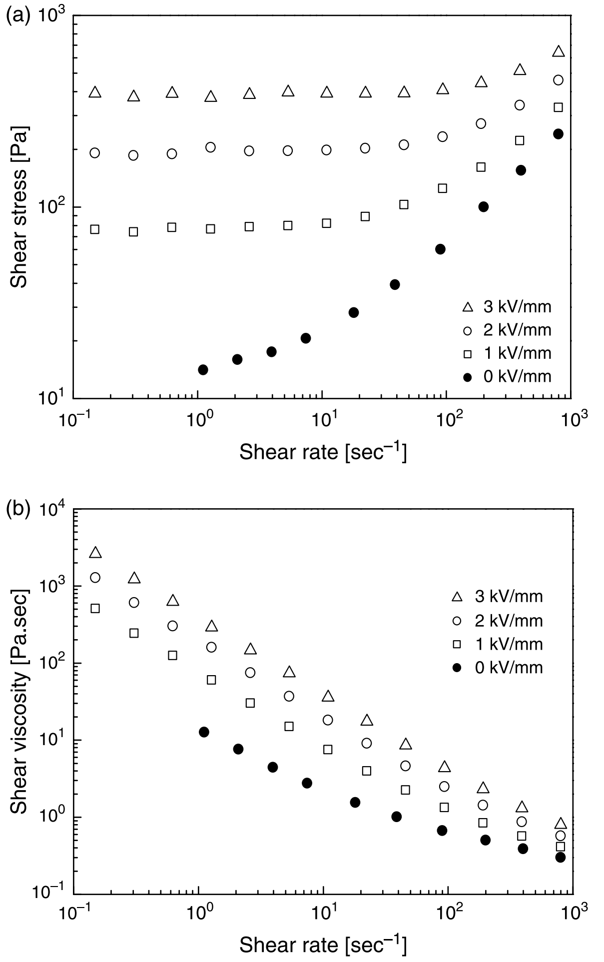

Fig. 2. Shear stresses (a) and viscosity (b) as a function of shear rate for 25 vol% PNQR in silicone oil under four different electric field strengths.

interaction is somewhat dominant before the shear rate reaches a critical value ($\dot{\gamma}_{\rm crit}$). After $\dot{\gamma}_{\rm crit}$, the hydrodynamic interaction gradually prevailed the electrostatic interaction with increasing shear rate, and the ER effect disappears completely at extremely high shear rate. This behavior has also been observed for various semiconducting, polymer-based ER fluids [35,36]. Therefore, the flow curves demonstrate the structural changes or deformation of the fluids caused by applied electric field and shear force.

Even though there have been extensive studies on quantitative analysis on both yield stress and shear stress behaviors [37–40], a few reports on the constitutive equation can be found [38,41–43]. Furthermore, it has been recently investigated that complicated shear stress behaviors are often observed such as plateau region over a wide shear rate range, the existence of minimum shear stress at relatively low shear rate [36,44] and coexistence region of liquid–solid like system [24]. In addition, many of previously reported constitutive equations are too complicated so that those are seldom used [42,43]. Therefore, the main goal of this work is to propose a model constitutive rheological equation of state for the ER fluids under an applied electric field instead of their quantitative interpretation.

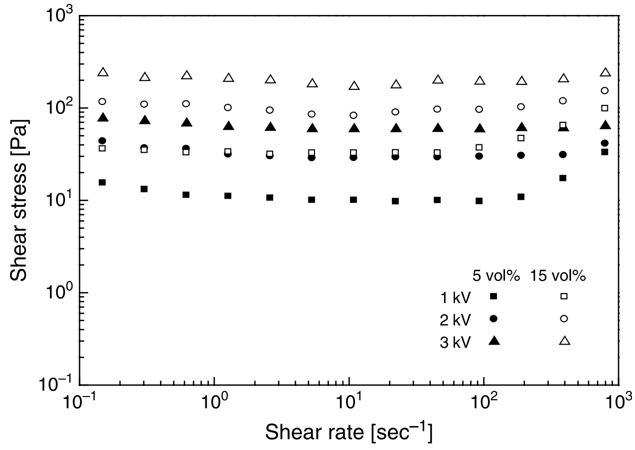

Fig. 3. Shear stresses as a function of shear rate for 5 and 15 vol% PNQR in silicone oil under three different electric field strengths.

Fig. 3 represents the flow curves for ER fluids (5 and 15 vol%) obtained from controlled shear rate mode under three different applied electric fields.

Three different models are used to analyze the shear stress distributions vs. shear rate. The lines in Fig. 4 are values calculated from the model equations.

Bingham model, shown in Eq. (1), is the simplest one with two parameters originating from yield stress τ_0 and Newtonian viscosity η_0 and is widely adopted as a model for ER suspensions (first category) (Fig. 5).

$$\tau = \tau_0 + \eta_0\dot{\gamma} \tag{1}$$

The Bingham model has two flow regimes; a rigid pre-yield behavior for shear stress less than the field-dependent yield stress and Newtonian flow characteristics beyond the yield stress τ_0 (post-yield region) [45]. Dotted lines in Fig. 4 are from Eq. (1) and deviate from the experimental data, especially for lower volume fractions of PNQR suspension.

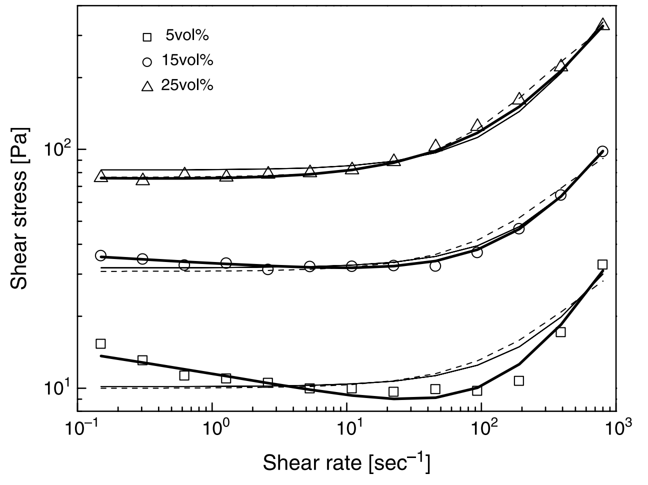

Fig. 4. Fit of model equations to flow curves for PNQR-based ER fluids with three different particle concentrations at the electric field strength of 1 kV/mm. Dashed line is for Bingham model (Eq. (1)), solid line for De Kee–Turcotte model (Eq. (3.a)), and bold solid line for our suggested model (Eq. (4)).

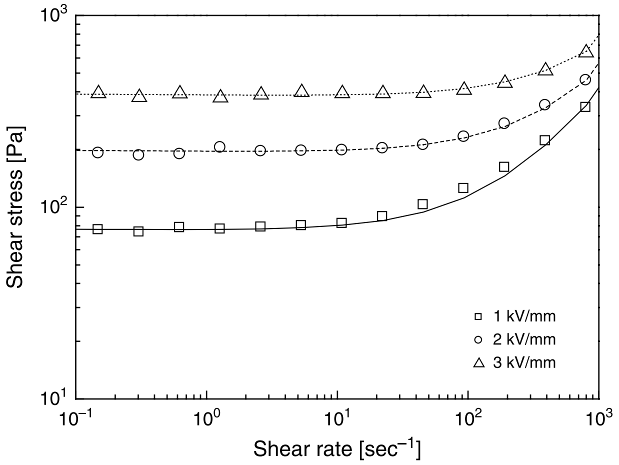

Fig. 5. Fit of our model (Eq. (4)) to flow curves for 25 vol % PNQR-based ER fluid.

The generalization of Eq. (1) can be expressed as:

$$\tau = \tau(\dot\gamma) + \eta(\dot\gamma)\dot\gamma \tag{2}$$

The second category will assume $\tau(\dot\gamma)$ to be independent of $\dot\gamma$ (i.e. $\tau(\dot\gamma) = \tau_0 =$ constant) and adopt various expressions for $\eta(\dot\gamma)$. Two commonly used forms are [46]:

$$\tau = \tau_0 + \eta_1\dot\gamma e^{-t_1\dot\gamma} \quad \text{(De Kee–Turcotte model)} \tag{3.a}$$

$$\tau = \tau_o + m\dot\gamma^n \quad \text{(Herschel–Bulkley model)} \tag{3.b}$$

where t_1 is a time constant having a unit of second. In fitting our data, we adopted the De Kee–Turcotte model.

A suggested model, given below, provides a better fitting of the PNQR-based ER fluids as following;

$$\tau = \frac{\tau_0}{1 + (t_2\dot\gamma)^\alpha} + \eta_\infty\left(1 + \frac{1}{(t_3\dot\gamma)^\beta}\right)\dot\gamma \tag{4}$$

The above six-parameter model can cover the stress decrease phenomena at low shear rate region and provide an accurate value for the real yield stress in the case of PNQR-based ER fluids. The first term in Eq. (4) implies the shear stress behavior at a low shear rate region especially in the case of the decrease of shear rate and the second term describes well the shear stress behavior at a high shear rate region.

Here, τ_0 is the dynamic yield stress defined as the extrapolated stress from low shear rate region, α is related to the decrease in the stress, t_2 and t_3 are time constants, and η_∞ is the viscosity at a high shear rate and is interpreted as the viscosity in the absence of an electric field. The exponent β has the range $0 < \beta \le 1$, since $d\tau/d\dot\gamma \ge 0$. The yield stresses and the optimal parameters for these three models are summarized in Table 1.

It was found from the results in Table 1, which the coefficients, α increase with increase in the particle concentration. The applied electric field strength gave the same effects on the α as the particle concentration. The β are 0.8, 0.5, and 0.1 for 5, 15, and 25 vol% of PNQR suspensions, respectively. From these results, 5 vol% PNQR is found to become a Newtonian fluid in high shear rate region. Furthermore, it can be found that the yield stresses obtained from both Bingham and De Kee–Turcotte models for 5 vol% PNQR are much lower than that from our model. This can be explained from the fact that while our model accurately fit the decrease of shear stress in the region of shear rate from 0.01 to 100 (1/s), other two models do not fit it well, so that as can be seen from Fig. 4, large deviation is observed at a very low shear rate from other two models.

Table 1
The optimal parameters in each model equation obtained from the flow curve of PNQR-based ER fluids at the electric field strength of 1 kV/mm

Model	Parameters	5 vol% PNQR	15 vol% PNQR	25 vol% PNQR
Bingham	τ_0	10.14	31.89	81.90
	η_0	0.025	0.082	0.325
De Kee–Turcotte	τ_0	9.98	30.81	76.31
	η_1	0.034	0.123	0.517
	t_1	0.0005	0.0006	0.00065
Eq. (4)	τ_0	18.0	35.0	75.0
	t_2	0.2	0.01	0.001
	α	0.3	0.7	3.0
	η_∞	0.032	0.08	0.2
	t_3	0.1	0.01	0.05
	β	0.8	0.5	0.1

Compared to several common methods for calculating the shear stress based on the mismatch ratio of the particle dielectric constant to that of the host liquid in an ac electric field or the ratio of the particle conductivity to that of the host fluid in a dc electric field, we proposed our empirical rheological equation of state not only for our PNQR-based ER fluids (Fig. 5) but also for many other ER fluids with any complicated flow curves of shear stress as a function of shear rate [47].

4. Conclusion

Suspensions of three different volume fractions of PNQR, dispersed in silicone oil, exhibited typical ER characteristics under an applied electric field. Flow behavior of PNQR-based ER fluids exhibited the micro-structural property changes during flow. Flow curves for each suspension obtained from the controlled shear rate mode, are categorized into plateau and Newtonian regions. The steady-state flow properties of PNQR-based ER fluids were interpreted by using three different models: Bingham, De Kee–Turcotte, and our model. Among these models, only our model fit the decrease in stress at the low shear rate regime accurately.

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References

[1] Gulley GL, Tao R. Phys Rev E 1997;56:4328.
[2] Davis LC. J Appl Phys 1997;81:1985.
[3] Parthasarathy M, Klingenberg DJ. Mater Sci Eng 1996;R17:57.
[4] Zhang Y, Lu K, Rao G, Tian Y, Zhang S, Liang J. Appl Phys Lett 2002;80:888.
[5] Mitsumata T, Sugitani K. Macromol Rapid Commun 2004;25:848.
[6] Mitsumata T, Sugitani K, Koyama K. Polymer 2004;45:3811.
[7] See H, Kawai A, Ikazaki F. Rheol Acta 2002;41:55.
[8] Lee HG, Choi SB, Han SS, Kim JH, Suh MS. Int J Mod Phys 2001;15:1017.
[9] Hao TJ. Colloid Interface Sci 1998;206:240.
[10] Yoshimoto S. Macromol Rapid Commun 2005;26:857.
[11] Cho MS, Choi HJ, Kim KY, Ahn WS. Stud Surf Sci Catal 2003;146:523.
[12] Choi HJ, Cho MS, Jhon MS. Int J Mod Phys B 1999;13:1901.
[13] Mezzasalma SA, Koper GJM. Colloid Polym Sci 2002;280:160.
[14] Choi HJ, Cho MS, To K. Physica A 1998;254:272.
[15] Woo DJ, Suh MH, Shin ES, Lee CW, Lee SH. J Colloid Interface Sci 2005;288:71.
[16] Kim JW, Choi HJ, To K. Polym Eng Sci 1999;39:1493.
[17] Kim JW, Choi HJ. J Korean Phys Soc 1999;35:S612.
[18] Block H, Kelly JP, Qin A, Waston T. Langmuir 1990;6:6.
[19] Choi HJ, Sim IS, Jhon MS. J Mater Sci Lett 2000;19:1629.
[20] Trlica J, Sáha P, Quadrat O, Stejskal J. Physica A 2000;283:337.
[21] Goodwin JW, Markham GM, Vinent B. J Phys Chem 1997;B101:1961.
[22] Kim JW, Jang LW, Choi HJ, Jhon MS. J Appl Polym Sci 2003;89:821.
[23] Lu J, Zhao XP. J Colloid Interface Sci 2004;273:651.
[24] Park SJ, Cho MS, Lim ST, Choi HJ, Jhon MS. Macromol Rapid Commun 2005;26:1563.
[25] Kim JW, Kim SG, Choi HJ, Jhon MS. Macromol Rapid Commun 1999;20:450.
[26] Chotpattananont D, Sirivat A, Jamieson AM. Colloid Polym Sci 2004;282:357.
[27] Yavuz M, Unal HI. J Appl Polym Sci 2004;9:1822.
[28] Choi HJ, Lee YH, Kim CA, Jhon MS. J Mater Sci Lett 2000;19:533.
[29] Kim SG, Choi HJ, Jhon MS. Macromol Chem Phys 2001;202:521.
[30] Gao ZW, Zhao XP. Polymer 2003;44:4519.
[31] Choi HJ, Cho MS, Jhon MS. Polym Adv Technol 1997;8:697.
[32] Wu CW, Conrad H. J Mater Res 1998;13:3299.
[33] Tanaka K, Ichizawa K, Onishi Y, Kubono A, Akiyama R. Int J Mod Phys B 2002;16:2683.
[34] Kim SG, Kim JW, Jang WH, Choi HJ, Jhon MS. Polymer 2001;42:5005.
[35] See H. J Ind Eng Chem 2004;10:1132.
[36] Cho MS, Cho YH, Choi HJ, Jhon MS. Langmuir 2003;19:5875.
[37] Martin JE, Anderson RA. J Chem Phys 1996;104:4814.
[38] See H. J Phys D: Appl Phys 2000;33:1625.
[39] Tam WY, Yi GH, Wen W, Ma H, Loy MMT, Sheng P. Phys Rev Lett 1997;78:2987.
[40] Duan X, Chen H, He Y, Luo W. J Phys D: Appl Phys 2000;33:696.
[41] Brunn PO, Abu-Jdayil B. Rheol Acta 2004;43:62.
[42] Wang B, Xiao Z. Acta Mechanica 2003;163:99.
[43] Eckart W. Continuum Mech Thermodyn 2000;12:341.
[44] See H, Kawai A, Ikazaki F. Colloid Polym Sci 2002;280:24.
[45] Kim YD, Park DH. Synth Met 2004;142:147.
[46] Carreau PJ, De Kee DCR, Chhabra RP. Rheology of polymeric systems; principles and application. Cincinnati: Hanser/Gardner; 1997.
[47] Pavlinek V, Saha P, Kitano T, Stejskal J, Quadrat O. Physica A 2005;353:21.