

Influence of Irradiation Crosslinking on the Self-Heating and Conduction of an Acetylene Carbon Black Filled High-Density Polyethylene Composite in the Electric–Thermal Equilibrium State

Yihu Song, Qiang Zheng

Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education),
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 20 April 2007; accepted 5 June 2007

DOI 10.1002/app.26959

Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The electric self-heating and conduction behaviors of a high-density polyethylene/acetylene carbon black composite crosslinked with electron-beam irradiation are studied with respect to the electric field and ambient temperature. On the basis of scaling arguments, the critical fields and current densities for the onsets of self-heating

and global electrical breakdown are discussed with respect to the intrinsic resistivity at a given ambient temperature as well as the irradiation dosage. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3009–3013, 2008

Key words: composites; fillers; polyethylene (PE)

INTRODUCTION

Composites of semicrystalline polymers and conducting particles show positive temperature coefficient effects of resistivity over a temperature range around the melting point (T_m) of the matrix.^{1–6} In important industrial applications to self-regulating heaters, the applied electric current is quite large, so marked self-heating is generated.^{7–11} These composites possess nonlinear conduction characteristics^{12–14} under a quite high electric field that modifies the electrical contact of the particles and thus restricts the current passing through samples. This leads to a global resistance increase with time until a switched electric–thermal equilibrium state is reached.¹⁵ In the electric–thermal equilibrium state, the rates of heat generation and heat dissipation are equal, so both the current passing through the sample and the sample temperature due to self-heating do not vary with time.^{10,16–18} In a nonlinear current density/electric field (J – E) plot, a maximum value of the current density (J) reveals the global breakdown of the electrical contact between the particles.^{19–21} The dynamic process of conduction switching has attracted considerable attention in recent years.^{10,11,16–24}

The negative temperature coefficient effect of resistivity above T_m has an adverse influence on the application of positive temperature coefficient com-

posites because of the conduction instability. Irradiation crosslinking of the matrix can eliminate the negative temperature coefficient effect and result in stable conductive behavior.⁷ In a previous article,¹⁷ we studied the self-heating and nonlinear conduction in the electric–thermal equilibrium state for a high-density polyethylene (HDPE)/acetylene carbon black (CB) composite. In this article, we further investigate the influence of irradiation crosslinking on the self-heating and conduction behaviors in the electric–thermal equilibrium state for HDPE/CB composites subjected to a wide electric field strength (E) range above room temperature yet well below T_m .

EXPERIMENTAL

The preparation of HDPE/CB composites with a CB volume fraction of 0.082 and electron-beam irradiation are described in an earlier article.²⁵ The simultaneous measurement of the sample surface temperature (T_s) and current in the electric–thermal equilibrium state as a function of the sinusoidal alternating-current (50 Hz) voltage at desired ambient temperatures (T_a 's) was performed at least 10 min after an alternating-current voltage was applied to the sample, as described previously.¹⁷

RESULTS AND DISCUSSION

Figure 1 shows T_s as a function of E for the composites at various values of T_a . Self-heating is absent at low E , whereas T_s increases steeply with increasing E above the critical field strength (E_c), depending on

Correspondence to: Y. Song (s_yh0411@zju.edu.cn).

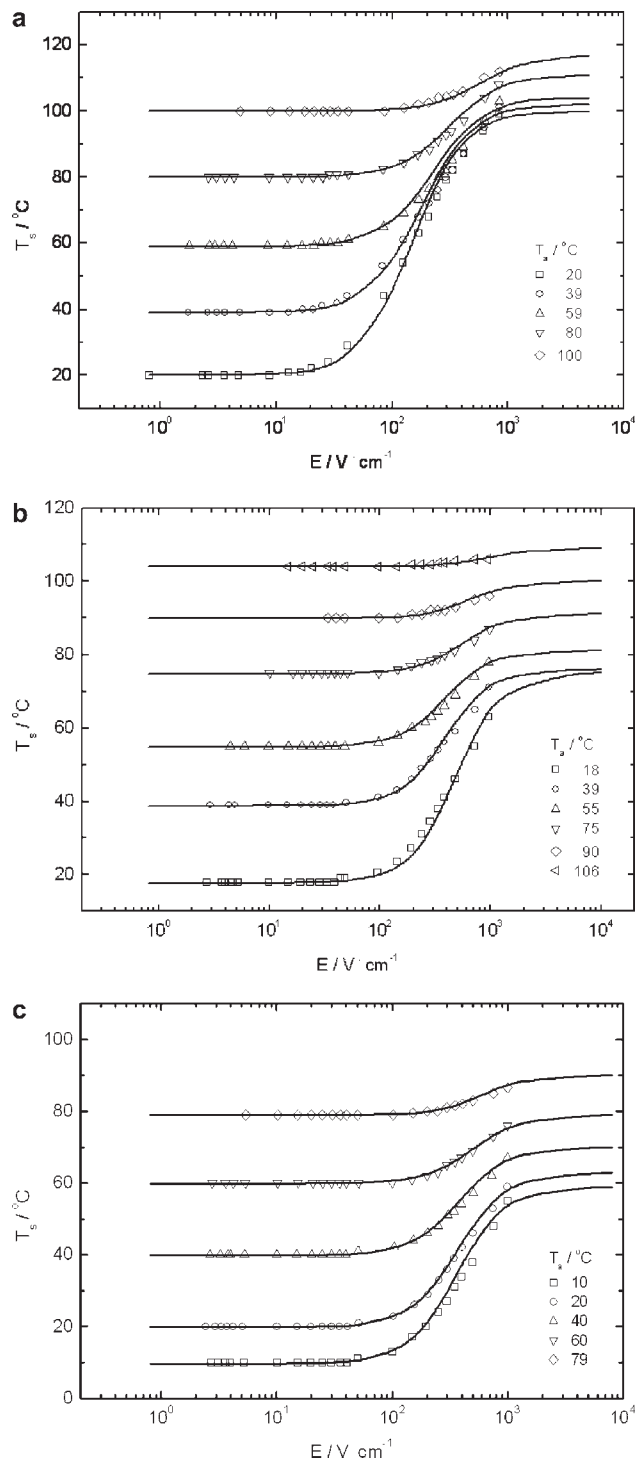


Figure 1 T_s measured at the sample surface as a function of E for the HDPE/CB composites crosslinked with irradiation doses of (a) 8, (b) 40, and (c) 200 kGy at various values of T_a . The solid curves were calculated according to eq. (3).

T_a . Figure 2 presents the nonlinear J - E characteristics in the electric-thermal equilibrium state. With increasing T_a , J is gradually lowered at the same level of E because of the increase in the intrinsic resistivity (ρ_0). When $E_{0.5}$ and $J_{0.5}$ (the coordinates at

the crossover point) at the global breakdown of the electrical contact between the particles are used as scaling variables, the normalized current density ($J/J_{0.5}$) as a function of the normalized field strength ($E/E_{0.5}$) collapses onto respective master curves for the composites crosslinked with irradiation dosages of 8, 40, and 200 kGy, as shown in Figure 3, and this

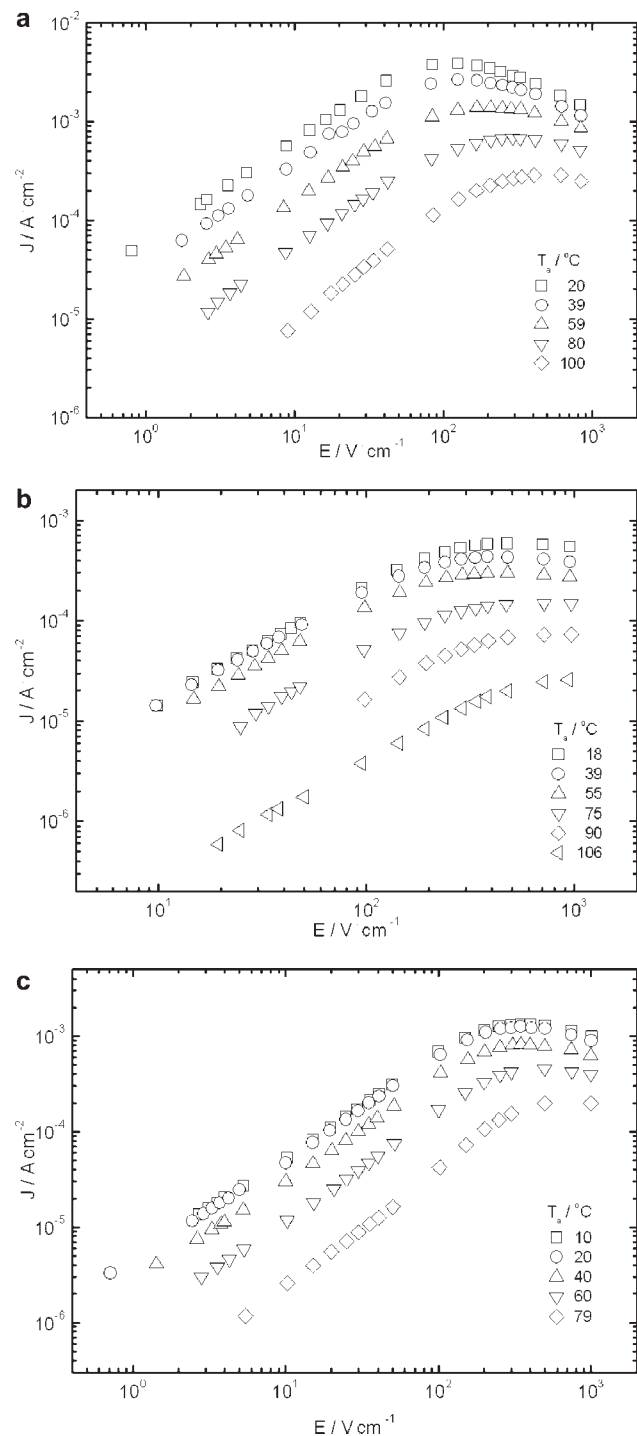


Figure 2 J - E characteristics for the HDPE/CB composites crosslinked with irradiation doses of (a) 8, (b) 40, and (c) 200 kGy at various values of T_a .

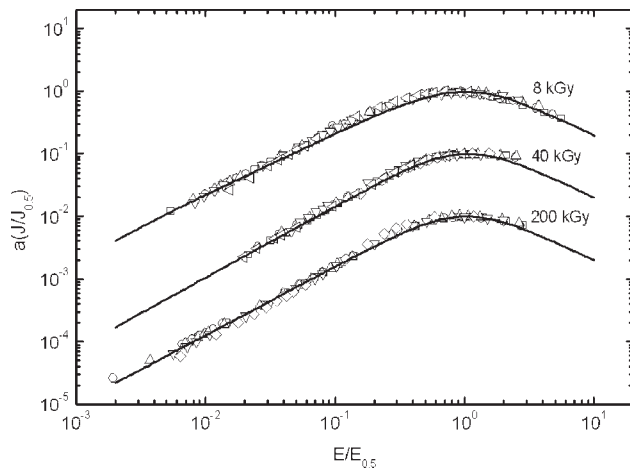


Figure 3 $J/J_{0.5}$ as a function of $E/E_{0.5}$ for the HDPE/CB composite at various values of T_a . The solid curves were calculated according to eq. (5). The data for the 40- and 200-kGy samples are shifted along the vertical axis by factors of $a = 10^{-1}$ and $a = 10^{-2}$, respectively.

suggests that the occurrence of nonlinear J - E characteristics is independent of crosslinking.

In Figure 1, E_c for the self-heating effect (E_c can be experimentally determined as a temperature rise of $T_s - T_a = 1^\circ\text{C}$) is shifted to high fields with increasing T_a . E_c and the corresponding current density (J_c) are plotted against ρ_0 in Figure 4. Mukherjee et al.²⁶ showed that the following scaling laws are applicable to conducting composites, and they obtained $p = q = 0.5$ under a mean-field approximation:

$$E_c \sim \rho_0^p \tag{1}$$

$$J_c \sim \rho_0^{-q} \tag{2}$$

The values of p and q have been estimated from the slopes in Figure 4 and are plotted against the irradiation dosage in Figure 5. p and q are close to each other and vary within the narrow range of 0.33–0.49, which is comparable to that of 0.45 ± 0.01 obtained by Mukherjee et al. for HDPE/carbon composites with filler concentrations above the percolation threshold. The crosslinking of the matrix does not influence p and q significantly. In other words, the onset of self-heating is mainly involved in the initial topology of the percolating network whenever the self-heating effect does not appear.

If we assume that the resistance variation with respect to T_s follows an exponential relation, an analysis of the electric-heating equilibrium between heat generation and heat dissipation under a nonohmic approximation gives a theoretical expression of T_s as a function of E .¹⁰

$$T_s - T_a = (T_{sm} - T_a) \frac{\left(\frac{E}{E_{0.5}}\right)^{2\alpha}}{1 + \left(\frac{E}{E_{0.5}}\right)^{2\alpha}} \tag{3}$$

Here, α is a nonlinear exponent sensitive to the filler type, and T_{sm} is the saturated value of the surface temperature at a high field limit. According to the Fourier law, the temperature rise ($T_s - T_a$) is proportional to the electrical power (EJ) in the electric-thermal equilibrium state, which can be formulated in terms of scaled variables ($J/J_{0.5}$ and $E/E_{0.5}$):

$$T_s - T_a = \frac{(T_{sm} - T_a)}{2} \left(\frac{E}{E_{0.5}}\right) \left(\frac{J}{J_{0.5}}\right) \tag{4}$$

Comparing eqs. (3) and (4) leads to a theoretical expression of $J/J_{0.5}$ as a function of $E/E_{0.5}$:¹⁷

$$\frac{J}{J_{0.5}} = \frac{2\left(\frac{E}{E_{0.5}}\right)^{2\alpha-1}}{1 + \left(\frac{E}{E_{0.5}}\right)^{2\alpha}} \tag{5}$$

Equation (5) has been used to fit the data in Figure 3, and the results are shown as solid curves. The α values have been determined to be 0.99, 1.07, and 1.05, respectively, for the composites crosslinked

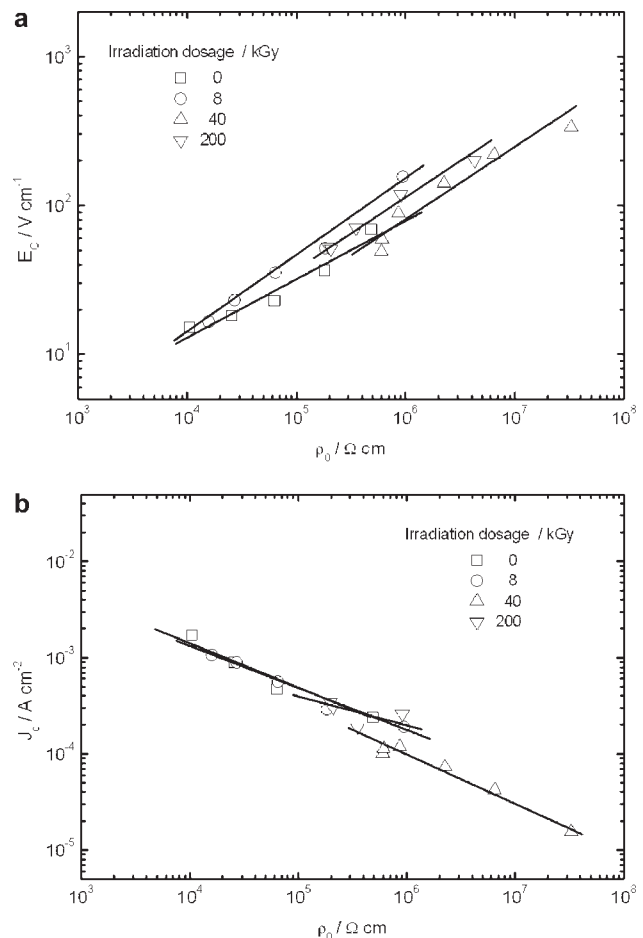


Figure 4 (a) E_c and (b) J_c as functions of ρ_0 . The lines in parts a and b are fitted according to eqs. (1) and (2), respectively.

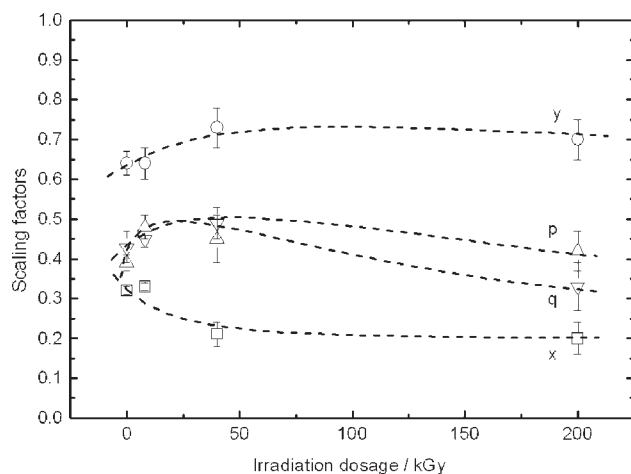


Figure 5 Scaling factors x , y , p , and q as functions of the irradiation dosage. The dotted curves are guides for the eyes.

with irradiation dosages of 8, 40, and 200 kGy, and they are essentially the same as the value of 1.10 found for the uncrosslinked composite at $T_a \leq 100^\circ\text{C}$.¹⁷ The α values, very close to unity, suggest that the conduction at $E \ll E_{0.5}$ is mainly ohmic and that the crosslinking of the matrix does not influence the conduction mechanism. Using the determined α values, we applied eq. (3) to fit the data in Figure 1. The best fitting results are shown as solid curves, and they well account for the general tendency of T_s as a function of E . $T_{sm} - T_a$, characterizing the maximum self-heating ability, is plotted against ρ_0 in Figure 6. It reveals that the crosslinking of the matrix improves the maximum self-heating ability at the same value of ρ_0 , whereas the temperature rise is less than 10°C at $\rho_0 > 10^7 \Omega \text{ cm}$.

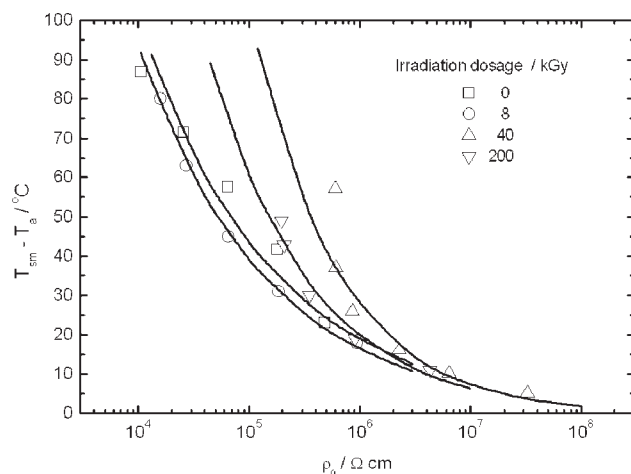


Figure 6 Maximum temperature rise ($T_{sm} - T_a$) at high E as a function of ρ_0 . The solid curves were calculated according to eq. (9).

Figure 7(a,b) shows $E_{0.5}$ and $J_{0.5}$ as functions of ρ_0 . In a random resistor network (RRN), each resistor has a breaking current above which the resistor becomes an insulator.^{27,28} If a sufficiently low voltage is applied, the system behaves just as an RRN in the ordinary percolation framework. On the other hand, some of the resistors will break under a sufficiently high voltage, and this leads to a redistribution of current on the remaining resistors and thus causes them to break in succession, resulting in the global electric breakdown.²⁹ The critical field ($E_{0.5}$) and current density ($J_{0.5}$) scale with ρ_0 as follows:¹⁷

$$E_{0.5} \sim \rho_0^x \quad (6)$$

$$J_{0.5} \sim \rho_0^{-y} \quad (7)$$

The application of eqs. (6) and (7) to the data in Figure 7 gives the scaling factors x and y , as shown in Figure 5. A theoretical analysis based on the RRN model has yielded $y \approx 0.85$.^{30,31} However, the y value in the HDPE/CB composites is not a constant

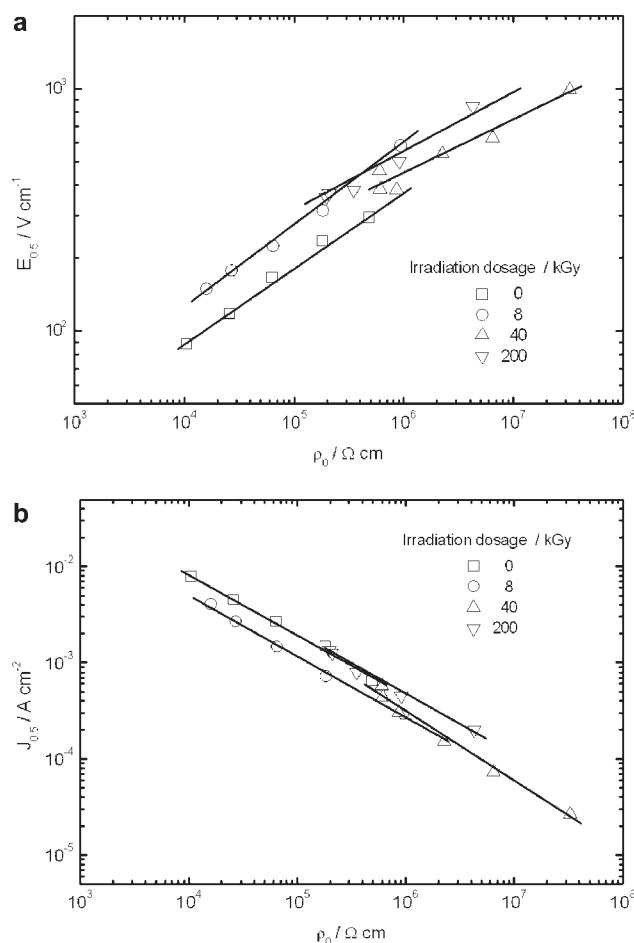


Figure 7 (a) $E_{0.5}$ and (b) $J_{0.5}$ as functions of ρ_0 . The lines in parts a and b are fitted according to eqs. (6) and (7), respectively.

but varies slightly within the narrow range of 0.64–0.73. It seems that an increasing irradiation dosage leads to an increase in y . The variation of x shows a contrary tendency with respect to the irradiation dosage. The application of a high field to the sample might lead to local melting of thin HDPE layers between CB particle pairs. The presence of interchain crosslinks restricts the local rearrangement of the particles and hinders the local breakdown, and this is the reason that x and y level off at high irradiation dosages.

$T_{sm} - T_a$ can be related to $E_{0.5}J_{0.5}$ as follows:¹⁷

$$T_{sm} - T_a = 2KE_{0.5}J_{0.5} \quad (8)$$

where K is a constant including the geometry of the sample and the heat dissipation to the surroundings. Combining eqs. (6)–(8), we obtain the following:

$$T_m - T_a \sim \rho_0^{x-y} \quad (9)$$

which suggests that the maximum self-heating ability decreases with increasing ρ_0 . With the determined values of x and y , eq. (9) approximately describes the general dependence of $T_{sm} - T_a$ on ρ_0 for the uncrosslinked and crosslinked composites at various values of T_a , as shown by the solid curves in Figure 6.

CONCLUSIONS

The crosslinking of the matrix through electron-beam irradiation does not influence the mechanisms of the self-heating and nonlinear conduction of HDPE/CB composites in the electric–thermal equilibrium state. However, crosslinking improves the maximum self-heating ability at the same value of ρ_0 . The critical fields and current densities for the onsets of self-heating and global electrical breakdown are involved in the crosslinking degree and T_a .

References

1. Meyer, J. *Polym Eng Sci* 1973, 13, 462.
2. Narkis, M.; Ram, A.; Flashmer, F. *Polym Eng Sci* 1978, 18, 649.
3. Narkis, M.; Ram, A.; Stein, Z. *J Appl Polym Sci* 1980, 25, 1515.
4. Kohler, F. U.S. Pat. 3,243,753 (1966).
5. Ohe, K.; Natio, Y. *Jpn J Appl Phys* 1977, 10, 99.
6. Bueche, F. *J Appl Phys* 1973, 44, 532.
7. Meyer, J. *Polym Eng Sci* 1974, 13, 706.
8. Oakes, J. A.; Sandberg, C. L. *IEEE Trans Ind Gen Appl* 1973, 9, 462.
9. Narkis, M. *Mod Plast* 1983, 60, 96.
10. Song, Y.; Pan, Y.; Zheng, Q.; Yi, X. *J Polym Sci Part B: Polym Phys* 2000, 38, 1756.
11. El-Tantawy, F.; Kamada, K.; Ohnabe, H. *Polym Int* 2002, 51, 635.
12. Kimura, T.; Yasuda, S. *Polymer* 1988, 29, 526.
13. Celzard, A.; Furdin, G.; Mareche, J. F.; McRae, E. *J Mater Sci* 1997, 32, 1849.
14. Amin, M.; Hassan, H. H.; Abdel-Bary, E. M. *J Polym Sci Polym Chem Ed* 1974, 12, 2651.
15. Lamaignere, L.; Carmona, F.; Sornette, D. *Phys Rev Lett* 1996, 77, 2738.
16. Song, Y.; Zheng, Q. *Polym Int* 2004, 53, 1517.
17. Song, Y.; Zheng, Q. *J Polym Sci Part B: Polym Phys* 2005, 43, 2484.
18. Song, Y.; Zheng, Q. *J Appl Polym Sci* 2005, 99, 1124.
19. de Arcangelis, L.; Hansen, A.; Herrmann, H. J.; Roux, S. *Phys Rev B* 1989, 40, 877.
20. Sahimi, M.; Arbabi, S. *Phys Rev Lett* 1992, 68, 608.
21. Acharyya, M.; Chakrabarti, B. K. *Phys Rev E* 1996, 53, 140.
22. El-Tantawy, F.; Bakry, A.; El-Gohary, A. R. *Polym Int* 2000, 49, 1670.
23. El-Tantawy, F.; Kamada, K.; Ohnabe, H. *J Appl Polym Sci* 2003, 87, 97.
24. El-Tantawy, F.; Dishovsky, N. *J Appl Polym Sci* 2004, 91, 2756.
25. Song, Y.; Zheng, Q. *Eur Polym J* 2005, 41, 2998.
26. Mukherjee, C. D.; Bardhan, K. K.; Heaney, M. B. *Phys Rev Lett* 1999, 83, 1215.
27. Rammal, R.; Tannous, C.; Breton, P.; Tremblay, A. M. S. *Phys Rev Lett* 1985, 54, 1718.
28. Rammal, R.; Tremblay, A. M. S. *Phys Rev Lett* 1987, 58, 415.
29. Duxbury, P. M.; Leath, P. L.; Beale, P. D. *Phys Rev B* 1987, 36, 367.
30. de Arcangelis, L.; Redner, S.; Herrmann, H. J. *J Phys Lett* 1985, 46, 585.
31. Bowanm, D. R.; Stround, S. *Phys Rev B* 1989, 40, 4641.