ELSEVIER

European Polymer Journal 37 (2001) 1871–1875

EUROPEAN
POLYMER
JOURNAL

www.elsevier.nl/locate/europolj

Conformational inversion of polyethylene–polyvinyl acetate graft copolymer in selective solvents by viscometry

J.W. Qian [*], G.H. Zhou, W.Y. Yang

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 27 March 2000; received in revised form 31 August 2000; accepted 13 March 2001

Abstract

Viscometric measurements were performed for a low molecular weight polyethylene (LMWPE) and the LMWPE grafted vinyl acetate (E-g-VA) copolymer in a series of binary solvent mixtures, consisting of a polar and a non-polar solvents. The degree of grafting (DG) or VA content dependence of the intrinsic viscosity $[\eta]$, Huggins constant k_H, and the critical association concentration C_A, of the polymers are investigated in the 1,2-dichloroethane (DCE)/cyclohexane (CYH) solvent mixtures, especially in $\Phi_c = 0.3$ and $\Phi_c = 0.9$ (Φ_c is the volume fraction of CYH in solvent mixtures). The opposite variations of $[\eta]$, k_H and C_A with the increasing of DG of the polymers studied at 30°C were observed in different solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively. Moreover, the inversion variation of $[\eta]$ of E-g-VA graft copolymer and its parent polymer (LMWPE) occurred with the change of the composition of the solvent mixtures. A large difference of the viscous flow energy of the E-g-VA graft copolymers from two different kinds of solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively was also found. These phenomena can be accounted for by the conformational inversion of the E-g-VA graft copolymer in the selective solvents.

Keywords: Graft copolymer; Viscosity; Core-shell transition; Conformational inversion and solvent effect

1. Introduction

It has been known that functionalization of polyolefins for use in blending or other applications and for its good qualities such as the light, UV and radiation resistance, weatherability, thermal stability, permeation of gases, permeability toward organic solutes, adhesive bond strength, impact resistance and the morphology of the polymer films etc. can be achieved by the grafting of vinyl monomers [1–16]. The studies of solution property of PE grafting copolymer were few in literatures although the solution properties of other kinds of graft copolymers were investigated extensively using light scatter and fluorescence mostly, also using DSC, UV, NMR and viscometry [17–24] etc.

We have even studied pour point depression and viscosity reduction of crude oil doped some graft copolymers [25]. And also, an E-g-VA grafting copolymer was prepared and worked for pour point depression of wax solutions [26]. In present work, the shape and its changing of the E-g-VA graft copolymer in solvent mixture of selective solvents of 1,2-dichloroethane (DCE) and cyclohexane (CYH) are investigated by viscometry.

2. Experimental

The low molecular weight polyethylene (LMWPE) was provided by Jinshan Petrochemical Company in Shanghai and purified with benzene (good solvent) and methanol (non-solvent) at room temperature. The E-g-VA graft copolymers used in this work were prepared with the purified LMWPE (5 g) in xylene (20 ml) at 70°C

---

[*] Corresponding author.
E-mail address: qianjw@ipsm.zju.edu.cn (J.W. Qian).

0014-3057/01/$ - see front matter
PII: S0014-3057(01)00056-8

with stirring and refluxing by dropping addition of vinyl acetate monomer (5 ml) with BPO (0.5 g) for 20 h in N_2 ambiance [26]. The mixture of the graft copolymer and homopolymer was isolated using non-solvent, methanol and *n*-hexane respectively. The structure and vinyl acetate content or degree grafting (DG) of the polymers were confirmed and calculated by IR spectra of Nicolet-5Dx (FTIR) and a method [27] using the infrared absorbance ratio of characteristic absorption peaks of C=O and CH_2, i.e., $\mathrm{DG} = \mathrm{VA}\ (\mathrm{wt.\%}) = 6.80(A_{1740}/A_{1470})$. Thus the DG of E-g-VA graft copolymer A and B are 19.8% and 8.87% respectively. The number average molecular weights of the E-g-VA graft copolymer A, B and their parent LMWPE are 1120, 970 and 820 respectively characterized using a Knauer VPO instrument. Viscosity measurement of the solutions was conducted in an Ubbelohde viscometer at designed temperature with deviation of ±0.02°C. The reproducibility of efflux-time was ±0.05 s.

3. Results and discussion

3.1. Huggins constant k_H and intrinsic viscosity $[\eta]$

Figs. 1 and 2 show the variation of reduced viscosity η_{sp}/c as a function of the concentration c of the E-g-VA graft copolymer A (GA), graft copolymer B (GB) and their parent LMWPE in solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively. It is clearly seen that each curve of these polymer/solvent systems exists crossover phenomenon, i.e., a concentration at which the polymer chains start contact, this concentration, which was indicated by the vertical arrow in Figs. 1 and 2, was called second critical concentration c^{**} [28] or critical association concentration C_A [29], and displaying two approximately straight lines with different slopes. Thus, two extrapolation to $c = 0$ are possible which give two different intrinsic viscosity $[\eta]$ and Huggins constants k_H:$[\eta]^*$, k_H^* using the plot obtained above C_A and $[\eta]^{**}$, k_H^{**} using the plot obtained below C_A.

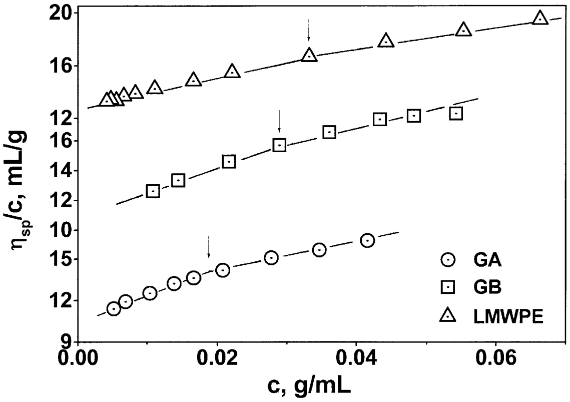

Fig. 2. Plot of the reduced viscosity of the graft copolymer GA, GB and their parent LMWPE vs the concentration in solvent mixture of $\Phi_c = 0.9$, (⊙) GA, (⊡) GB and (△) LMWPE.

The DG dependence of k_H^*, k_H^{**} and $[\eta]^*$, $[\eta]^{**}$ of the GA, GB and LMWPE in both solvents of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ are presented in Figs. 3 and 4, respectively. In Fig. 3, we observed that each system has a k_H value larger than 0.423 (the k_H of LMWPE in $\Phi_c = 0.9$ is 0.423), it means that each system is an association system. The k_H values, however, decreases and increases with the increasing of DG in solvent mixture of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively, i.e., the larger DG, the lower k_H value in $\Phi_c = 0.3$; and vice versa in $\Phi_c = 0.9$. That is to say, the aggregation occurred in solvent mixture of $\Phi_c = 0.3$ does not come from VA segments, in other

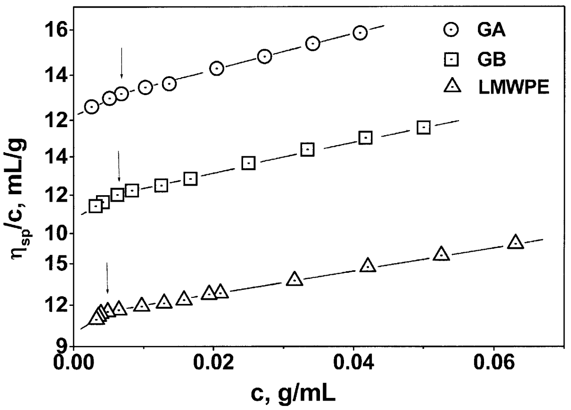

Fig. 1. Plot of the reduced viscosity of the graft copolymer GA, GB and their parent LMWPE vs the concentration in solvent mixture of $\Phi_c = 0.3$, (⊙) GA, (⊡) GB and (△) LMWPE.

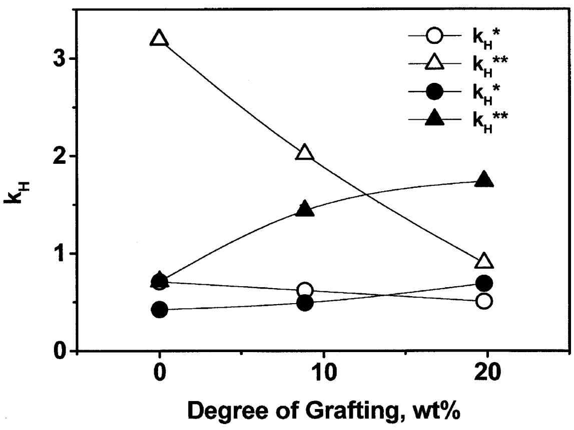

Fig. 3. Plot of Huggins constant k_H^* (circle) and k_H^{**} (triangle) vs DG of the polymers in solvent mixtures of $\Phi_c = 0.3$ (hollow) and $\Phi_c = 0.9$ (solid).

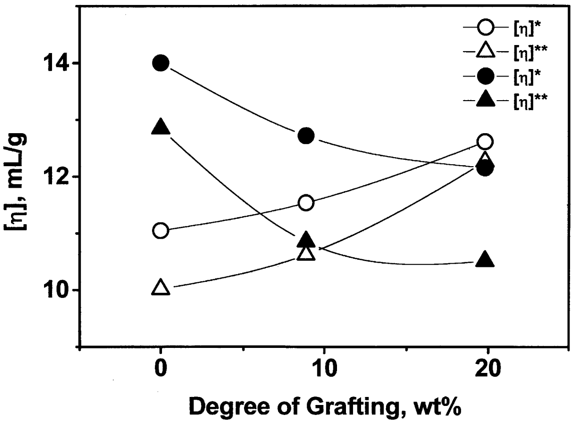

Fig. 4. Plot of intrinsic viscosity $[\eta]^*$ (circle) and $[\eta]^{**}$ (triangle) vs DG of the polymers in solvent mixtures of $\Phi_c = 0.3$ (hollow) and $\Phi_c = 0.9$ (solid).

words, the aggregation in $\Phi_c = 0.3$ comes from ethylene segment in E-g-VA graft copolymer molecule. Accordingly, the aggregation of the E-g-VA graft copolymer molecule in $\Phi_c = 0.3$ and $\Phi_c = 0.9$ are two different kinds of aggregations, one (in $\Phi_c = 0.3$) consist of ethylene segments, which was called ethylene segment aggregation; the other (in $\Phi_c = 0.9$) consist of VA segments aggregation which was called VA segment aggregation. Obviously, the reason for this is that DCE is a selective solvent that is a good solvent for VA segments and poor solvent for ethylene segments and CYH is also a selective solvent, but it is a good solvent for ethylene segments and poor solvent for VA segments.

Fig. 4 gives the variation of $[\eta]$ ($[\eta]^*$ and $[\eta]^{**}$) with DG in solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$, respectively. Clearly, the $[\eta]$ values go up with increasing of DG in $\Phi_c = 0.3$ due to the expending of more VA side chains and the increasing of the MW, both are caused by the increasing of DG in the E-g-VA graft copolymer molecule. It is interested that the $[\eta]$ values go down with increasing of DG in $\Phi_c = 0.9$. We consider that the coil shrinkage caused by more VA segment aggregation and further the ethylene segment aggregation is greater than the coil expansion caused by the increasing of MW. In Figs. 3 and 4, we can also observe that the variation of the $[\eta]^{**}$ and k_H^{**} are larger than those of $[\eta]^*$ and k_H^* with the increasing of DG. This could be more pronounced variation of the chain conformation in the case of lower solution concentration [30].

3.2. Critical association concentration C_A

Fig. 5 shows the relation between C_A and DG of the E-g-VA graft copolymer in both solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$. The variation of C_A values with DG is same as that of $[\eta]$ values with DG in Fig. 4. The C_A values increase with increasing of DG in $\Phi_c = 0.3$ and vice versa in $\Phi_c = 0.9$. As mentioned above, the aggregation of the graft copolymer in $\Phi_c = 0.3$ mainly comes from ethylene segment aggregation, then the aggregation of ethylene segment is getting harder due to the increasing DG or VA content in the E-g-VA molecules unless increasing the concentration of the E-g-VA graft copolymer. Thus, C_A rises. In opposition to $\Phi_c = 0.3$, the C_A in $\Phi_c = 0.9$ goes down with the increasing of the DG due to VA segment aggregation. It should be noted that the C_A values in solvent mixture of $\Phi_c = 0.9$ are much larger than those in solvent mixture of $\Phi_c = 0.3$ for the graft copolymer with the same DG. Prerri et al. [31] have pointed out that C_A value would be affected by the shape of macromolecular chain and the elongated chain has lower C_A value compared to the chains presenting coil conformation. Therefore, we can suppose that the E-g-VA molecule in solvent mixture of $\Phi_c = 0.3$ affords a conformation (I) of ethylene segment aggregation in core with the elongated VA side chain, and the E-g-VA molecule in solvent mixture $\Phi_c = 0.9$ renders a conformation (II) of VA segment aggregation in core with the coiled backbone chain.

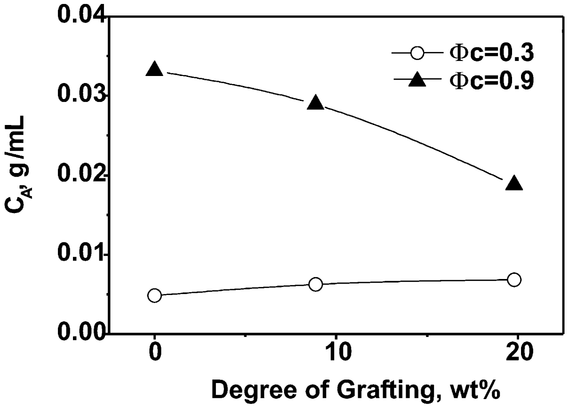

Fig. 5. Plot of critical association concentration C_A vs DG of the polymers in solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$.

Fig. 6 gives the influence of the composition of solvent mixture on the $[\eta]^*$ of E-g-VA graft copolymer A (○), B (□) and their parent polymer LMWPE (△) at 30°C. The ranges of composition of the solvent mixture are chosen from $\Phi_c = 0.3$ to $\Phi_c = 0.9$ in which the E-g-VA graft copolymer and their parent LMWPE are all dissolved. It shows that the slopes of the $[\eta]^* \sim \Phi_c$ lines for these three samples depress from positive to negative with the increasing of Φ_c. Thus, the $[\eta]$ values of these three samples in $\Phi_c = 0.3$ increase with increasing of DG of the samples and vice versa in $\Phi_c = 0.9$. Two crossovers are displayed by LMWPE line with GA and GB lines respectively. We believe that they are the inversion points from conformation (I) to conformation (II) when

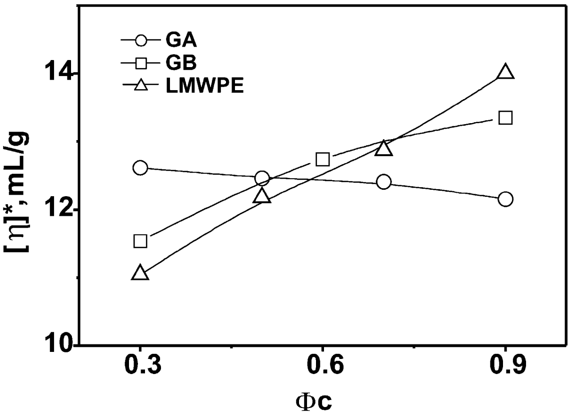

Fig. 6. Plot of $[\eta]^*$ vs the composition of solvent mixtures Φ_c for the polymers with different DG, (○) GA, (□) GB and (△) LMWPE.

the composition of solvent mixtures changes from $\Phi_c = 0.3$ to $\Phi_c = 0.9$ based on the different aggregated states of the E-g-VA molecule in the solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$. Further, the conformational inversion point of sample GA with increasing of DG is located in the solvent mixture with less Φ_c value compared to that of sample GB with increasing of DG. This is probably due to that more VA segments of E-g-VA graft copolymer need less non-solvent CYH in solvent mixture for the VA segment aggregation.

3.3. Viscous flow energy E_η

Fig. 7 shows the variation of $\ln \eta$ as a function of the temperature ($1/T$) obtained from the E-g-VA graft copolymer in solvent mixture of $\Phi_c = 0.3$ (hollow symbol) and $\Phi_c = 0.9$ (solid symbol), respectively. In each solvent mixture three straight lines of the graft copolymer A with different concentrations are revealed, i.e., two of them are for the solutions, the other one is for the pure solvent mixture of $\Phi_c = 0.3$ or $\Phi_c = 0.9$. The viscous flow energies E_η at different solution concentrations could be calculated from the slope of each straight line. Provided that E_η represents pure viscous flow energy of the graft copolymer sample A, i.e., deducting the effect of solvent mixture of $\Phi_c = 0.3$ or $\Phi_c = 0.9$, thus,

$$E_\eta = E_{\eta_c} - E_{\eta_0}$$

where E_{η_0} and E_{η_c} are the viscous flow energies for pure solvent mixture and for the solution of the E-g-VA graft copolymer A with the concentration.

Fig. 8 shows the concentration dependence of E_η of the E-g-VA graft copolymer A from the solvent mixture of $\Phi_c = 0.3$ and $\Phi_c = 0.9$, respectively. If we consider the points from solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ as lines roughly, the increments of E_η from the slopes of the lines are $E_{\eta_{0.3}} = 29.4$ kJ/mol and $E_{\eta_{0.9}} = 20.7$ kJ/mol for the solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$, respectively. It is interested that why the $E_{\eta_{0.3}}$ is larger than $E_{\eta_{0.9}}$ although the solvent effect is deducted. According to the viscous flow energies of PVA and PE with 67 and 25 kJ/mol respectively [32], this result is also a good evidence for two kinds of conformations of the E-g-VA graft copolymer in solvent mixture of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively. In solvent mixtures of $\Phi_c = 0.3$, the coil of E-g-VA molecule looks like PVA molecule, i.e., the core and shell of the coil are ethylene and VA segments respectively. In solvent mixtures of $\Phi_c = 0.9$, the coil of E-g-VA molecule looks like PE molecule, i.e., the core and shell of the coil are VA and ethylene segments, respectively. Accordingly, VA segments out of the coil in solvent mixture of $\Phi_c = 0.3$ displays stronger interaction between VA segment, VA segment and DCE molecule similar to the action in the mixture of ethylene–

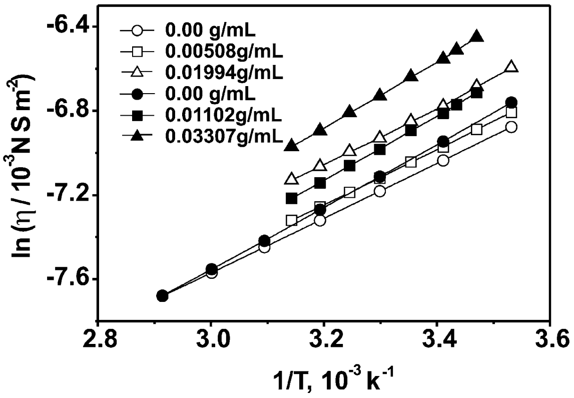

Fig. 7. Plot of $\ln \eta$ vs $1/T$ for GA sample in solvent mixtures of $\Phi_c = 0.3$ (hollow) and $\Phi_c = 0.9$ (solid) with different concentrations.

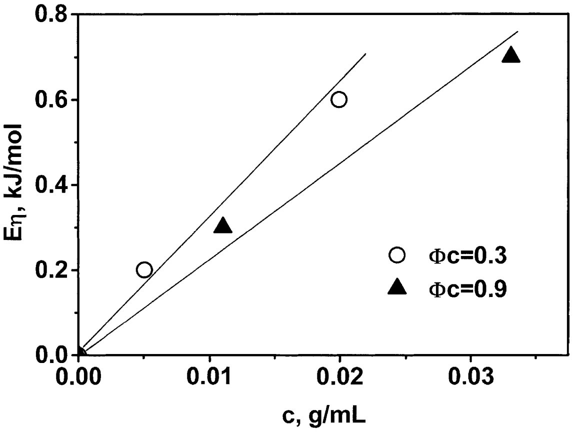

Fig. 8. Plot of E_η vs C for GA sample in solvent mixture of $\Phi_c = 0.3$ and $\Phi_c = 0.9$.

vinyl acetate copolymer with poly(vinyl chloride) [33] and resulting in higher E_η value. On the contrary, ethylene segments out of the coil in solvent mixture of $\Phi_c = 0.9$ render weaker interaction between ethylene segment, ethylene segment and CYH molecule, and resulting in lower E_η value.

The E-g-VA graft copolymer studied in this present investigation reduces the pour point of the waxy systems that is very much dependent on the nature of solvent as in the case of the pour point depressant of the ethylene–vinyl acetate (EVA) copolymer [34]. The aggregation of the EVA copolymer formed in solvent mixture of DCE/CYH with lower Φ_c values may cause a higher degree of pour point depression of waxy solutions.

4. Conclusions

The changes of the intrinsic viscosity, Huggins constant and critical concentration of the E-g-VA graft copolymers with the increasing of degree of grafting are opposite in selective solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ respectively; the ratios of $d[\eta]/d\Phi_c$ of the E-g-VA graft copolymers are from positive (DG = 0 or 8.87) to negative (DG = 19.8) gradually when the composition of the solvent mixtures change from $\Phi_c = 0.3$ (strong polar) to $\Phi_c = 0.9$ (weak polar); the viscous flow energy of the E-g-VA graft copolymer A is larger in $\Phi_c = 0.3$ ($E_{\eta_{0.3}} = 29.4$ kJ/mol) than that in $\Phi_c = 0.9$ ($E_{\eta_{0.9}} = 20.7$ kJ/mol). From these results we consider that two different aggregated states of the E-g-VA graft copolymer in selective solvent mixtures of $\Phi_c = 0.3$ and $\Phi_c = 0.9$ exist, i.e., (I) ethylene segment aggregated in core with the shell of VA segments and (II) VA segment aggregation in core with the shell of ethylene segments, respectively. And the conformation inversion of the E-g-VA graft copolymer is dependent on the quality of the solvent mixtures.

Acknowledgements

This work was made possible by the financial support from NSFC (no. 29774020).

References

[1] Liu NC, Baker E, Russell KE. J Appl Polym Sci 1990;41:2285.

[2] Simmons A, Baker WE. Polym Engng Sci 1989;29:1117.

[3] Wang H, Chen W. J Appl Polym Sci 1999;74(9):2150.

[4] Mehta IK, Kumar S, Chauhan GS, Misra BN. J Appl Polym Sci 1990;41:1171.

[5] Shrama YN, Naqvi MK, Gawande PS, Bhardwaj IS. J Appl Polym Sci 1982;27:2605.

[6] Bae YO, Ha CS, Cho WJ. Eur Polym J 1991;27(2):121.

[7] Gaylord NG, Mehta R. J Polym Sci, Part A: Polym Chem 1988;26:1189.

[8] Russell KE, Kelusky EC. J Polym Sci, Part A: Polym Chem 1988;26:2273.

[9] Sipos A, Mccarthy J, Russell KE. J Polym Sci, Part A: Polym Chem 1989;27:3353.

[10] Yamakawa S. J Appl Polym Sci 1976;20:3057.

[11] Kanitz PJF, Huang RYM. J Appl Polym Sci 1971;15:67.

[12] Yuee F, Tyagi S. J Membr Sci 1988;39:1.

[13] Dean BD. J Appl Polym Sci 1986;32:5619.

[14] Shibayama M, Hashimoto T, Kawai H. Macromolecules 1983;16:1434.

[15] Inoue T, Soen T, Hashimoto T, Kawai H. J Polym Sci, Polym Phys 1969;7:1283.

[16] Kamel I, Kusy RP, Corneliussen RD. Macromolecules 1973;6(1):53.

[17] Eckert AR, Webber SE. Macromolecules 1996;29:560.

[18] Papanagoulos D, Dondos A. Eur Polym J 1995;31(10): 977.

[19] Kotaka T, Tanaka T, Hattori M, Inagaki H. Macromolecules 1978;11:138.

[20] Watanabe A, Matsuda M. Macromolecules 1986;19: 2253.

[21] Watanabe A, Matsuda M. Macromolecules 1985;18:273.

[22] Geetha B, Mandal AB, Ramasami T. Macromolecules 1993;26:4083.

[23] Chujo Y, Shishino T, Tsukahara Y, Yomashita Y. Polym J 1985;17:133.

[24] Gosa K, Donescu D. Makromol Chem 1981;182:1725.

[25] Qian JW, Qi GR, Ding XZ, Yang SL. Fuel 1996;75(3): 307.

[26] Zhou GH, Qian JW, Li J, Qi GR. Polym Mater Sci Engng Sin, in press.

[27] French AK, Berham JV, Pullukat TJ. Appl Spectrosc 1974;28(5):477.

[28] Dondos A, Tsitsitianis C, Staikos G. Polymer 1989;30:690.

[29] Qian JW, Li J, Yang YS, Qi GR. Chin J Polym Sci 1998;16(4):327.

[30] Dondos A, Papanagopoulos D. Makromol Chem Rapid Commun 1993;14:7.

[31] Prerri E, Papanagopoulos D, Dondos A. Colloid Polym Sci 1997;275:709.

[32] Van Krevelen DW. Properties of polymers. NY: Elsevier Scientific Publishing; 1990. p. 469 (Chapter 15).

[33] Coleman MM, Moskala EJ, Painter PC, Walsh DJ, Rostami SR. Polymer 1983;24:1410.

[34] Qian JW, Wang XH, Qi GR, Wu C. Macromolecules 1997;30:3283.