Toughening PA1010 with a Functionalized Saturated Polyolefin Elastomer

HONGBING CHEN, BINGXIN YANG, HAOYU ZHANG

Laboratory 24, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 13002, People's Republic of China

ABSTRACT: Polyamide (PA)1010 is blended with a saturated polyolefin elastomer, ethylene-α-olefin copolymer (EOCP). To improve the compatibility of PA1010 with EOCP, different grafting rates of EOCP with maleic anhydride (MA) are used. The reaction between PA1010 and EOCP-*g*-MA during extrusion is verified through an extraction test. Mechanical properties, such as notched Izod impact strength, elongation at break, etc., are examined as a function of grafting rate and weight fraction of elastomer. It was found that in the scale of grafting rate (0.13–0.92 wt %), 0.51 wt % is an extreme point for several mechanical properties. Elastomer domains of PA1010/EOCP-*g*-MA blends show a finer and more uniform dispersion in the matrix than that of PA1010/EOCP blends. For the same grafting rate, the average sizes of elastomer particles are almost independent on the contents of elastomer, but for different grafting rates, the particle sizes are decreased with increasing grafting rate. The copolymer formed during extrusion strengthens the interfacial adhesion and acts as an emulsifier to prevent the aggregation of elastomer in the process of blending. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 928–933, 2000

Key words: PA1010; ethylene-α-olefin copolymer; grafting rate; mechanical properties; morphology

INTRODUCTION

Polymer blending is a simple and efficient way to produce high-performance polymer alloys. However, components should be selected properly, and processing conditions controlled strictly, so that suitable interfacial adhesion and proper morphology can be met.[1–7] Reactive extrusion is a widely used method to cause the formation of *in situ* copolymers. The copolymers created during extrusion can function as a bridge to connect two incompatible polymers. As a result, the interfacial tension is greatly reduced, and the morphology greatly changed.[8–10]

Polyamide (PA)6 and PA66 have been widely toughened by many elastomers. The rather important ones include EPDM and SEBE.[11–15] Before blending, elastomers were often grafted with maleic anhydride, acrylic acid, or glycidyl methacrylate monomers[16–18] to introduce active groups. Although functionalized EPDM and SEBS modifying nylon have achieved great success, the unsaturated double bond in EPDM and SEBS molecular chains could lower the aging property of their blends.

In this study, a new kind of saturated polyolefin, ethylene-α-olefin copolymer, and its derivant functionalized with maleic anhydride (EOCP-*g*-MA) are introduced to blend with PA1010. Good results have been achieved through reactive extrusion. The relationship between morphologies and mechanical properties and the effect of graft-

Table I   Blend Composition (wt %)

Sample	PA1010	EOCP-*g*-MA	Grafting Rate
NG1	95	5	0
NG3	85	15	0
NG5	75	25	0
PT1	95	5	0.51
PT3	85	15	0.51
PT5	75	25	0.51
PG3	85	15	0.13
AT3	85	15	0.92
PX3	85	15	0.30
BR3	85	15	0.71

ing rate on mechanical properties as well as morphologies are discussed.

EXPERIMENTAL

Materials and Blends Preparation

Polyamide 1010, commercially named SANLU A2, was purchased from Shanghai Celluloid Plant. EOCP was purchased from PULI Development Center of Polymer Materials in Beijing, China. Different grafting rates of EOCP-*g*-MA were prepared in our lab. PA1010 was vacuum-dried at 110°C overnight, and rubbers at 40°C overnight before use.

A ϕ30 co-rotating twin screw extruder (L/D = 28) was used to prepare blends at a screw speed of 100 rpm. The four barrel temperatures were set as 188, 200, 213, and 215°C.The extruding strands were pelletized after quenching in the air. Except for special annotation, all the percent contents refer to weight fractions. The codes and compositions of all blends investigated are reported in Table I.

Extraction Test

Before extraction, pellets of PA1010/EOCP (85: 15) and PA1010/EOCP-*g*-MA (85:15, grafting rate: 0.51%) were press-molded to thin films with 0.4 mm in thickness at 220°C. Films were extracted with xylene for 48 h. The final films were observed using a scanning electron microscope.

Mechanical Testing

Testing specimens for mechanical properties were prepared by using a JSWF17SA injector with barrel temperatures of 190, 200, and 210°C. An INSTRON 1121 was used to measure the tensile and flexural properties according to ISO/527-2: 1993(E) and ISO/178:1993(E), respectively. Izod impact strength tests were performed by means of an UJ-40 impact-testing machine on the basis of ISO/180:1993(E). Melt flow index (MFI) was performed at 230°C under a load of 0.325 kg.

Morphology Observation

A scanning electron microscope (JXA-840) was used to observe the morphologies of the blends. To distinguish elastomer phase from nylon phase, 0.07% of $KMnO_4$ solution in H_3PO_4/H_2SO_4 (volume ratio, 1:2) was used to selectively etch the elastomer phase of PA1010/EOCP-*g*-MA blends.

RESULTS AND DISCUSSION

Evidence of *In Situ* Composition

The Molau test has been widely used to investigate whether a graft copolymer has been formed during blending process.[3,10,17] In this article, a new method is suggested to confirm whether there is a graft copolymer formed in blending. Figure 1 shows the SEM micrographs of thin films of PA1010/EOCP and PA1010/EOCP-*g*-MA blends after extracting with xylene. Many holes can be found on the picture of NG3, but not on PT3. Xylene is a good solvent for EOCP but not for PA1010. In case of the EOCP domains were extracted, holes could remain. That is to say the EOCP domains can be easily removed from the nylon matrix for their weak adhesion with nylon. But because of the formation of new chemical bonds between PA1010 and EOCP-*g*-MA, the interfacial adhesion was greatly enhanced, and the EOCP domains cannot be extracted from the nylon matrix even for a rather long time.

Mechanical Properties

Effect of EOCP-g-MA Contents

Figure 2 shows the plots of notched Izod impact strength vs EOCP-*g*-MA or EOCP contents for PA1010/EOCP-*g*-MA and PA1010/EOCP blends. It is clearly seen that a transition from brittle to tough occurs for PA1010/EOCP-*g*-MA blends when the content of elastomer is 10%. But for PA1010/EOCP blends, their Izod impact strengths almost keep constant when the content of elastomer is up to 25%. This phenomenon was found
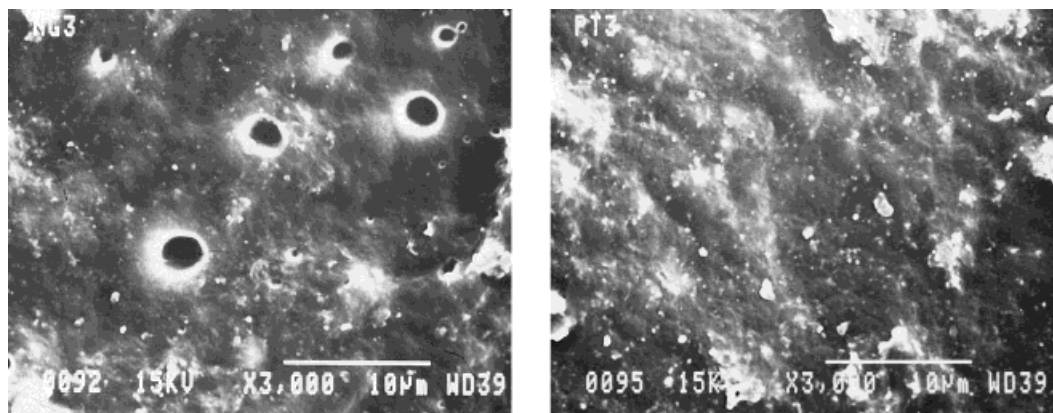
Figure 1   SEM micrographs for NG3 and PT3 films after extraction.

in many other blending systems and related to their different morphologies.[1,7,12] A detailed discussion is given below.

Effect of Grafting Rate

To study the effect of grafting rate on the mechanical properties, the EOCP-*g*-MA content is fixed at 15% in the PA1010/EOCP-*g*-MA blends. Table II shows the mechanical properties of EOCP-*g*-MA with different grafting rates modifying PA1010 blends. For the scale of different grafting rates of EOCP prepared in our lab, the brittle to tough transition always can be realized as long as the content of EOCP-*g*-MA has reached the critical value. Figure 3 shows the plot of the critical content of EOCP-*g*-MA to result in the brittle to tough transition vs grafting rate for PA1010/EOCP-*g*-MA blends and Figure 4 shows the plot of MFI value vs grafting rate. It is interesting to note that the elongation at break, MFI value and the critical content for brittle to tough transition both have extreme points at the grafting rate of 0.51%. It was reported[8,19] that the amino groups in nylon molecular chains can react with carboxyl of maleic anhydride and result in the formation of copolymer which functions as compatibilizer. This phenomenon is obviously related to the degree of such reaction. However, until now a suitable means to measure the reaction degree of this reaction has not been built because of the difficulty in finding a solvent for both PA1010 and EOCP. Therefore, further research is needed to discover whether there exists some inert regular pattern in this phenomenon.

Morphology

To study the morphologies, samples of PA1010/EOCP blends were frozen in liquid nitrogen for 15

min and then fractured for observation. For their strong interfacial adhesion, samples of PA1010/EOCP-*g*-MA blends were etched with 0.07% KMnO$_4$ solution in H$_3$PO$_4$/H$_2$SO$_4$ to remove the grafting elastomer domains. Figure 5 shows their morphologies. From these pictures, it is obvious that the average sizes of elastomer particles of PA1010/EOCP blends are much larger than that of PA1010/EOCP-*g*-MA blends. The average particle sizes are proportional to the elastomer contents for PA1010/EOCP blends, but not the same for PA1010/EOCP-*g*-MA blends. A balance exists between particle breakup and aggregation in the process of blending.[20,21] When the EOCP contents of PA1010/EOCP blends are increased, the aggregation of particles is enhanced for more chance of collision, and the balance is moved to the direction of particle aggregation, so the particle size is increased as the content of elastomer is increased. This tendency is shown in Figure 5 (NG1, NG3, NG5). For PA1010/EOCP-*g*-MA blends, the for-
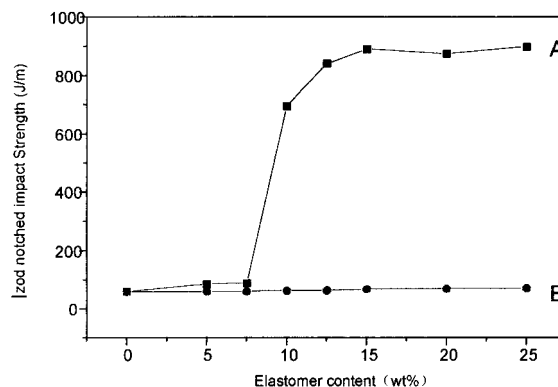

Figure 2   Izod notched impact strength as a function of elastomer content. (A) PA1010/EOCP-*g*-MA (grafting rate, 0.51%); (B) PA1010/EOCP.

Table II Elongation at Break (EB), Tensile Strength (σ_t), Young's Modulus (E_y), Flexural Strength (σ_f), and Flexural Modulus (E_f) of PA1010/EOCP-*g*-MA Blends

Sample	EB (%)	σ_t (MPa)	E_y (MPa)	σ_f (MPa)	E_f (MPa)
NG3	252.73	43.07	773.22	56.32	1029.6
PG3	272.22	49.33	767.83	53.23	955.04
PX3	259.90	45.89	704.61	47.61	867.54
PT3	247.62	46.06	750.76	48.87	863.40
BR3	250.07	44.77	725.48	46.60	859.57
AT3	268.31	47.21	687.30	50.59	906.78

mation of copolymer during extrusion behaved as an emulsifier to inhibit the aggregation of particles, and the inhibition effect predominated that balance, so the particle size was almost independent of the content of elastomer, which is shown in Figure 5 (PT1, PT3).

Compared with PT1 and PT3, sample PT5 gave a kind of co-continue morphology. This phenomenon can also be explained by the inhibition effect. In the PA1010/ EOCP-*g*-MA blending system, increasing the content of elastomer results in more particles formed for the nearly invariant particle diameter. When the number of elastomer particles reaches a critical value, particle connection will take place, and co-continue phase is formed. Small particle diameters correspond to low critical values, and large particle diameters to high values. That is why co-continue morphology cannot be seen in NG5 but is clearly shown in PT5.

With different grafting rates (0.13, 0.51, and 0.92%) but the same content (15%) of EOCP-*g*-MA, the morphologies of PA1010/EOCP-*g*-MA blends are shown in Figure 6. The average diam-

eters of holes left by EOCP-*g*-MA are decreased as the grafting rate is increased. This can be explained from the master curve: $G\eta_m\alpha/\gamma = 4P^{0.84}$, which was reported by Wu.[2] In our systems, the shear rate G, the matrix viscosity η_m, and the viscosity rate P of disperse phase to matrix are the same for the three blends; therefore, the average elastomer particle diameter α is inverse proportional to the interfacial tensions γ. With the increase of grafting rate, more functional groups take part in the reaction on the interface, and the interfacial tensions become weaker because more copolymers are generated during the process of blending. As a result, the elastomer particle sizes show a tendency to become smaller as the grafting rate increases.

CONCLUSIONS

The formation of PA1010-MA-*g*-EOCP grafting copolymer during reaction extrusion is verified through the extraction test. The copolymer
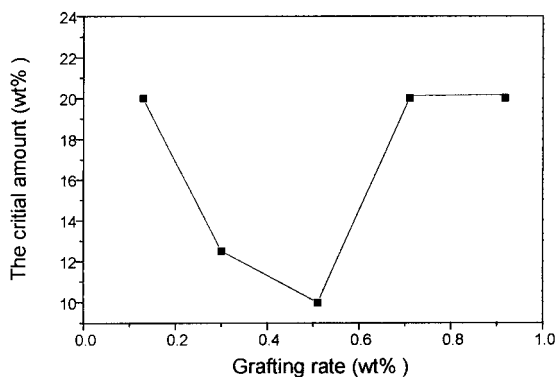

Figure 3 The critical content of PA1010/EOCP-*g*-MA as a function of the grafting rate for PA1010/EOCP-*g*-MA blends.
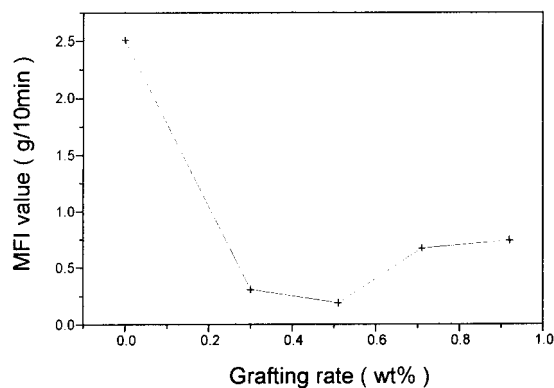

Figure 4 MFI values of PA1010/EOCP-*g*-MA as a function of grafting rate.
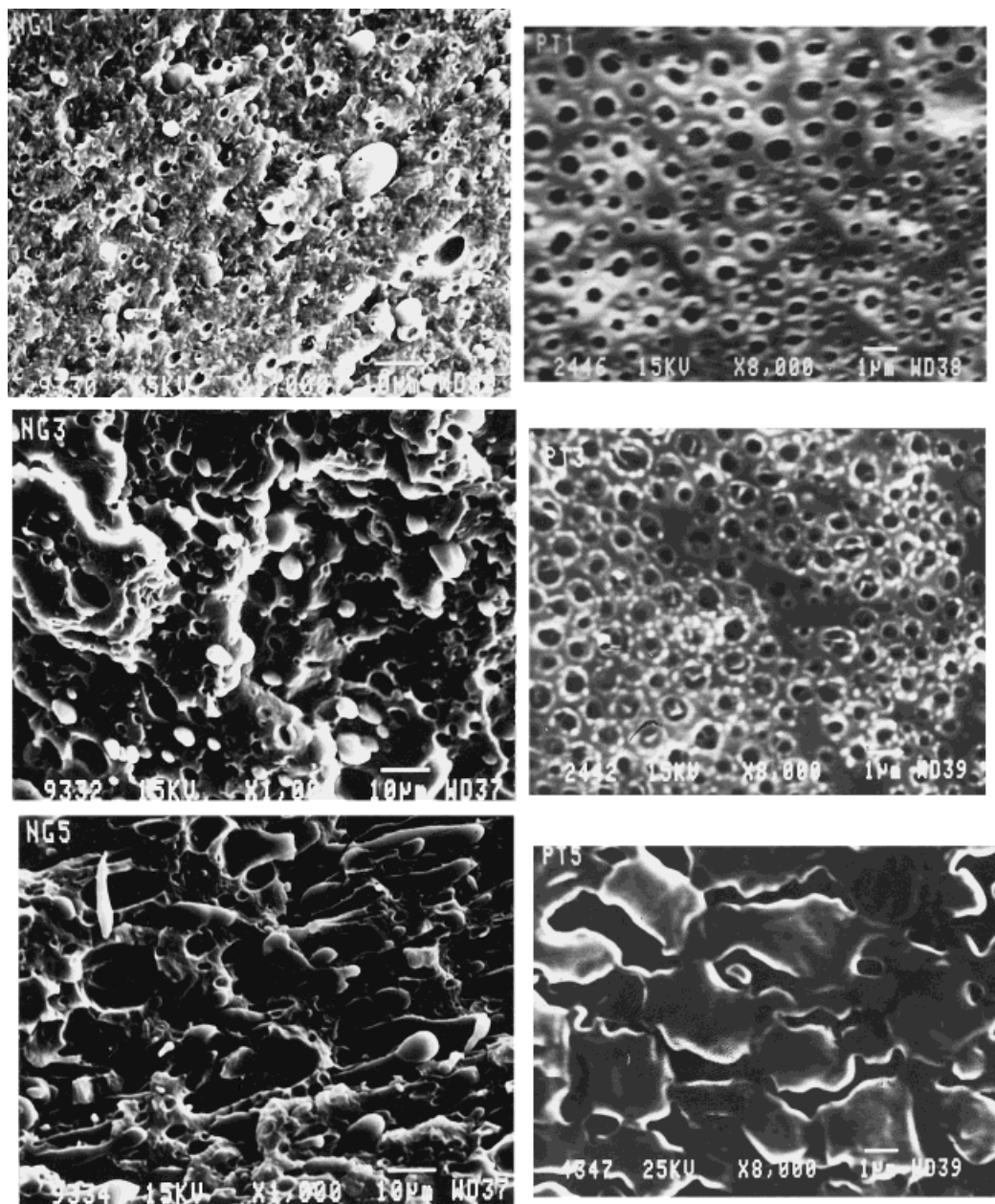
Figure 5 SEM micrographs for PA1010/EOCP and PA1010/EOCP-*g*-MA blends. NG1, NG3, and NG5 fractured in nitrogen; PT1, PT3, and PT5 etched with acid solution.

greatly enhanced the interfacial adhesion of PA1010 and EOCP. PA1010 can be greatly toughened by blending with functionalized EOCP, and different grafting rates have different critical contents resulting in the brittle to tough transition. Among the grafting rates listed in our study, 0.51% is an extreme point for several mechanical properties.

Mechanical properties of PA1010/EOCP-*g*-MA blends vary for different grafting rates of EOCP-*g*-MA. Different degrees of reaction between PA1010

and EOCP-*g*-MA during extrusion may be the cause for their difference of mechanical properties.

The copolymer formed during extrusion functions as an interfacial agent to lower the interfacial tension, improve the interfacial tension, and significantly reduce the minor particle size. For PA1010/EOCP blends, the average particle sizes are proportional to the contents of EOCP, but for the PA1010/EOCP-*g*-MA system, the average sizes almost keep constant with increased EOCP-
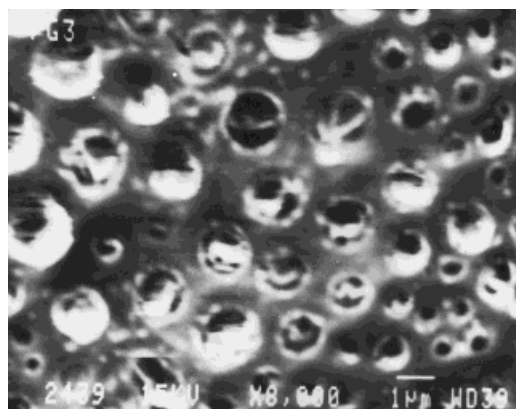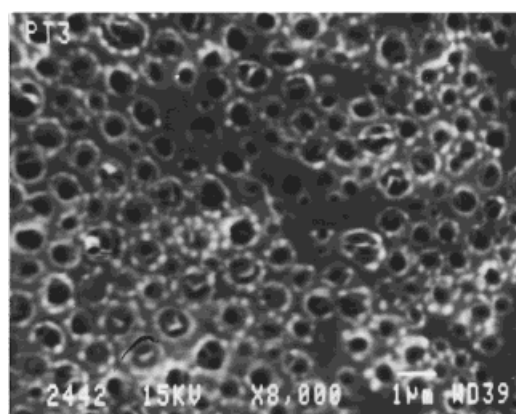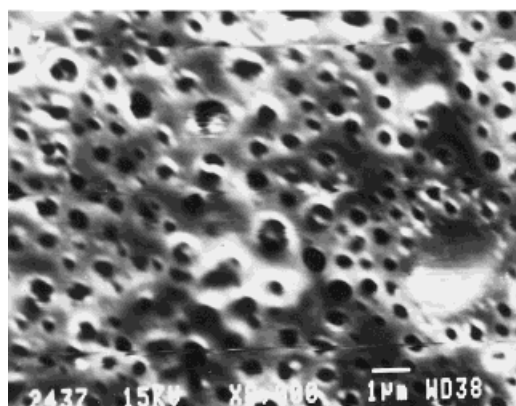
Figure 6 SEM micrographs for (a) PG3, (b) PT3, and (c) AT3 etched with acid solution.

g-MA content. The copolymer formed through extrusion between PA1010 and EOCP-*g*-MA greatly prevents the particles' aggregation. The dimensions of elastomer are inverse proportional to the grafting rate in the scale of 0.13–0.92% for PA1010/EOCP-*g*-MA blends because more copolymer formed in the interface would lead to lower interfacial intense.

REFERENCES

1. Wu, S. Polymer 1985, 26, 1855.
2. Wu, S. Polym Eng Sci 1987, 27, 335.
3. Borggreve, R. J. M.; Gaymans, R. J.; Schuijer Polymer 1989, 30, 71.
4. Wu, S. Polym Eng Sci 1990, 30, 753.
5. Majumdar, B.; Keskkula, H.; Paul, D. R. Polymer 1994, 35, 1386.
6. Muratoglu, O. K.; Argon, A. S.; Cohen R. E.; Weinberg, M. Polymer 1995, 36, 921.
7. Oshinski, A. J.; Keskkula; Paul, D. R. J Appl Polym Sci 1996, 61, 623.
8. Horicuchi, S.; Matchariyakul, N.; Yase, K.; Kitano, T. Macromolecules 1997, 30, 3664.
9. Zhang, X.; Li, X.; Wang, D. J Appl Polym Sci 1997, 64, 1489.
10. Molau, G. E.; Kolloid, Z. Z. Polymer 1970, 238, 493.
11. Wu, S. J Polym Sci Polym Phys Ed 1983, 21, 699.
12. Majumadar, B.; Keskkula, H.; Paul, D. R. J Appl Polym Sci 1994, 54, 339.
13. Greco, R.; Malinconic, M.; Martuscelli, E.; et al. Polymer 1987, 28, 1185.
14. Oshinski, A. J.; Keskkula, H.; Paul, D. R. Polymer 1992, 33, 268.
15. Takeda, Y.; Keskkula, H.; Paul, D. R. Polymer 1992, 33, 3173.
16. Yin, Z.; Zhang, Y.; Zhang, X.; Yin, J. J Appl Polym Sci 1997, 63, 1565.
17. Illing, G. Angew Makromol Chem 1981, 95, 83.
18. Yu, Z.; Ou, Y.; Qi, Z.; Hu, G. J Polym Sci Part B Polym Phys 1998, 36, 1987.
19. Minoura, Y.; Ueda, M.; Mizunuma, S.; Oba, M. J Appl Polym Sci 1969, 13, 1625.
20. Sundararaj, U.; Macosko, C. W. Macromolecules 1995, 28, 2647.
21. Hu, G.; Kadri, I. J Polym Sci Part B Polym Phys 1998, 36, 2153.