

Structure–Property Relationships of Lightly Chemical Crosslinked Poly(vinyl chloride) Thermoplastic Elastomer

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Received 17 August 1998; accepted 30 August 1999

ABSTRACT: Chemical crosslinked poly(vinyl chloride) (C-PVC) was synthesized by vinyl chloride suspension polymerization in the presence of diallyl phthalate (DAP) and plasticized to prepare poly(vinyl chloride) (PVC) thermoplastic elastomer (TPE) materials. The chemical crosslinking and physical crosslinking structure in chemical crosslinked PVC-TPE were investigated. It showed that the gel fraction and the crosslinking density of gel increased as the feed concentration of DAP increased. C-PVC prepared by VC/DAP copolymerization was lightly crosslinked as compared with irradiation crosslinked PVC. Physical entanglements would greatly influence the crosslinking density of gel when the gel fraction was high. Chemical crosslinking had little influence on the recrystallization behavior of PVC. A structure model of chemical crosslinked PVC-TPE was proposed, in which chemical networks acted with physical networks cooperatively. It also showed that chemical crosslinking and physical crosslinking influenced the processability and mechanical properties of chemical crosslinked PVC-TPE cooperatively. Although the processability of PVC-TPE deteriorated with chemical crosslinking, the dimension stability and elasticity of PVC-TPE were improved as the permanent chemical networks were introduced. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 868–874, 2000

Key words: poly(vinyl chloride); thermoplastic elastomer; chemical crosslinking; physical crosslinking; elasticity

INTRODUCTION

Plasticized poly(vinyl chloride) (PVC) exhibits rubberlike elasticity, and the most reasonable explanation is the presence of a physical network consisting of small crystallites.^{1–3} However, plasticized PVC suffers from certain drawbacks, such as bad elasticity compared with crosslinked rubber, low softening temperature and poor dimensional stability at increased temperature.

An obvious way to overcome these deficiencies of plasticized PVC is to introduce a permanent chemical network. This may be done, for example,

by irradiation crosslinking in the presence of sensibilizers and crosslinking aids.^{4,5} Alternatively, a crosslinking agent (such as divinyl monomer) or a difunctional nucleophile agent can be used to introduce crosslinks in PVC during its processing.^{6–9} These crosslinking methods always cause the accelerated thermal degradation of PVC and the difficulty to reprocess due to its high crosslinking density. It has been found that chemical crosslinked PVC could be prepared by vinyl chloride (VC) suspension polymerization in the presence of divinyl monomer and be easy to control the structure of chemical crosslinked PVC by varying the concentration of divinyl monomer in feed.¹⁰ PVC obtained was always lightly chemical crosslinked and exhibited reprocessability and improved elasticity after plasticization, which

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Journal of Applied Polymer Science, Vol. 76, 868–874 (2000)
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qualified it to be used as a thermoplastic elastomer (TPE). Although the synthesis of chemical crosslinked PVC by VC/divinyl monomer copolymerization had been reported in many patents,¹¹ the structure and properties of lightly chemical crosslinked PVC-TPE were seldomly studied till now.

In this paper, a series of lightly chemical crosslinked PVC resin will be prepared by VC/diallyl phthalate (DAP) suspension copolymerization and plasticized to prepare TPE materials. The structure and properties of lightly chemical crosslinked PVC-TPE will be investigated.

EXPERIMENTAL

Materials

VC was polymerization grade. DAP was supplied by Shuguang Chemical Company of Shanghai, China, and purified before use. Dicyclohexyl peroxycarbonate used as initiator was washed twice with methyl alcohol before use. Hydroxypropylmethylcellulose (65SH50) and partially hydrolyzed poly(vinyl alcohol) (KH20) were products of Synthesis Chemical Co. of Japan and used as suspending agents. S1000 PVC was supplied by Qilu Petrochemical Co., China. Tribasic lead sulphate (TBLS), lead stearate, and di-2-ethylhexyl phthalate (DEHP) were used as heat stabilizer, lubricant, and plasticizer for PVC processing, respectively, and were all commercial products.

Synthesis and Characterization of PVC

PVC resin was synthesized in a 5-L jacketed autoclave equipped with an agitator in the suspension process. Polymerization temperature was well controlled by water bath and the polymerization conversion was controlled to be 75–85%.

The gel fraction (w_g) of PVC was determined by Soxhlet extraction with tetrahydrofuran (THF). PVC gel was swollen in THF and the crosslinking density (ν) of gel was calculated from the degree of swelling according to the Flory-Rehner equation,¹²

$$\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2 = -\nu V_1\nu_2^{1/3}$$

in which ν_2 is the volume fraction of gel in swollen system, χ is the interaction parameter of PVC and THF ($\chi = 0.14$; Ref. 13), and V_1 is the molar volume of THF.

The polymerization degree of PVC sol was calculated from the viscosity of its dilute solution in nitrobenzene according to the National Standard of China: GB/T-5761-93.

Processing and Analysis of PVC-TPE

One hundred parts PVC, 5.0 parts TBLS, 1.0 part lead stearate, and 80 parts DEHP were mixed and two-roller milled to obtain PVC-TPE material. The recrystallization behavior of plasticized PVC was investigated on Perkin-Elmer DSC7 differential scanning calorimeter, the test method was described earlier.¹⁴ The degree of crystallinity (X_c) of PVC was calculated according to the following equation:

$$X_c = \frac{\Delta H}{\Delta H_u} \times 100\%$$

where ΔH was the crystallite fusion enthalpy of PVC sample tested by DSC, and ΔH_u was the fusion enthalpy of 100% crystalline PVC. ΔH_u was determined to be 10.5 cal/g by Anagnostopoulos et al.¹⁵ and Patterson et al.¹⁶; this value was used in this paper.

The rheological behavior of plasticized PVC powder was measured in the System-90 Haake torque rheometer. The set temperature of mixing chamber was 165°C, the speed of rotors 40 rpm, and the charge 67.0 g. The rheological behavior of PVC-TPE was also characterized in the capillary rheometer after the first processing. The capillary with $L/D = 40$ was used, the shear rate and apparent viscosity were calculated without entrance and exit correction.

PVC-TPE sample pieces were prepared by compression molding and used to test mechanical properties. Heat-deformation measurement was applied to evaluate the dimension stability of PVC-TPE. The penetration value of a loaded probe was recorded using an instrument made by ourselves. The tip of the probe was flat with a surface area of 7.07 mm² and the weight was 244.5 g (0.34 N/mm²), the heating rate was about 2°C. The permanent compression set was measured according to the Japanese Standard JIS K-6301. The sample was compressed to about 25% strain in a designed jig, and placed in a bake oven at temperature of 70°C for 22 h. The permanent compression set was calculated from the initial strain and the strain after the above treatment.

Table I Effects of Synthesis Factors on the Structure of PVC

	Polymerization Temperature (°C)	f_0 of DAP (mmol/mol VC)	Gel Fraction (%)	DP of sol	ν of Gel (10^{-5} mol/cm ³)
C0	45	0	0	1732	—
C1	45	0.505	8.73	2790	0.23
C2	45	0.667	32.7	1634	0.44
C3	45	0.783	43.7	1404	0.65
C4	45	1.010	53.1	1038	0.95
C5	45	1.015	55.5	1060	1.06
C6	45	1.523	72.1	656	1.62
C7	45	2.513	88.9	253	5.53
C8	50	0.503	7.5	2756	0.18
C9	50	0.622	24.4	1095	0.38
C10	50	0.911	30.1	800	0.40
C11	50	0.995	50.9	679	0.97
C12	50	2.025	80.0	344	2.94
C13	60	0.637	18.5	1165	0.26
C14	60	1.089	32.0	1065	0.44
C15	60	1.523	55.0	646	0.99
C16	60	2.477	76.0	465	2.01

RESULTS AND DISCUSSION

Characterization of Chemical Crosslinked PVC Resin

Chemical crosslinked PVC was synthesized by VC/DAP suspension copolymerization and characterized by the gel fraction (w_g), the degree of polymerization (DP) of sol and the crosslinking density (ν) of gel. Effects of the feed concentration (f_0) of DAP and polymerization temperature on the gel fraction, DP of sol, and crosslinking density of gel are shown in Table I.

Table I shows that the gel fraction and crosslinking density increase as the f_0 of DAP increases at the same polymerization temperature, but the DP of sol decreases. The crosslinking density shown in Table II is much lower than that

of irradiation crosslinked PVC,⁴ which means that only lightly crosslinked PVC is prepared by VC/DAP copolymerization.

Figure 1 shows the relationships of the gel fraction and the crosslinking density of gel for different chemical crosslinked PVC. It can be seen that the crosslinking density of gel increases slowly with increasing of gel fraction when the gel fraction is low, and increased rapidly when the gel content is high (>70%).

The crosslinking density calculated from the degree of swelling is the elastically effective crosslinking density, which includes the contribution of chain entanglements. As shown in Figure 2, chain entanglements can be classified into five kinds according to the situations of their connection in four directions. According to Langley's en-

Table II X_c and T_m of PVC-TPE After Annealing Treatments (Annealing Temperature: 125°C)

Annealing Time (min)	C0 ($w_g = 0$)		C2 ($w_g = 32.7\%$)		C6 ($w_g = 72.1\%$)	
	X_c (%)	T_m (°C)	X_c (%)	T_m (°C)	X_c (%)	T_m (°C)
10	1.3	137.6	1.2	137.7	1.1	137.9
20	1.8	139.7	1.6	139.6	1.5	139.1
30	2.1	140.0	2.0	140.2	1.9	140.2
60	2.8	141.0	2.2	141.2	2.1	141.3
90	3.0	141.6	2.6	141.8	2.4	141.9

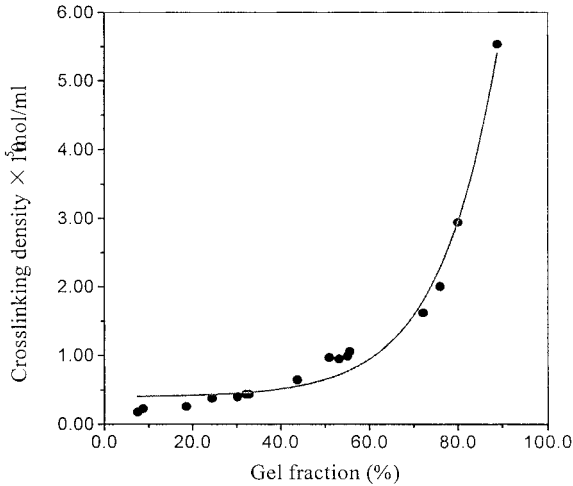


Figure 1 The relationship of gel fraction and the crosslinking density of gel for crosslinked PVC.

tanglement entrapment criteria,¹⁷ only the fifth kind of chain entanglements that have four directions lead to gel segments, are elastically effective, and contribute to the crosslinking density. With the Flory criterion,¹⁸

$$\nu = \nu_c w_g T_e^{1/2} + \nu_e T_e$$

where ν_c is the chemical crosslinking density, w_g is the gel fraction, ν_e is the concentration of potential entanglements, and T_e is the fraction of potential entanglements that have become trapped by the chemical crosslinking process. T_e is proportional to the fourth power of gel fraction, so chain entanglements have great contribution to ν when the gel fraction is high.

Recrystallization Behavior of Chemical Crosslinked PVC-TPE

Crystallites have great effects on the flow, viscoelastic behavior and mechanical properties of

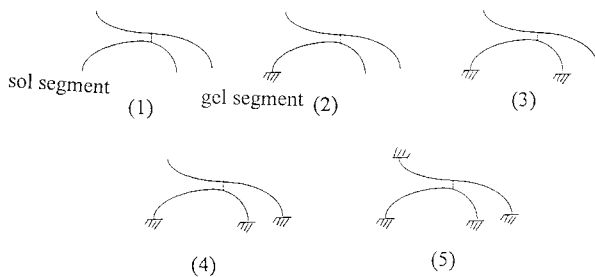


Figure 2 Classification of chain entanglements.

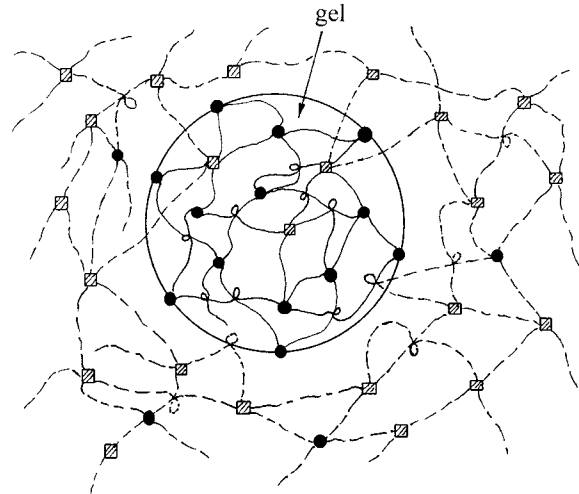


Figure 3 The structure model of plasticized and crosslinked PVC. ●: Chemical crosslinking point; ▨: microcrystallite crosslinking point; ○: entanglement point.

PVC. The annealing process was used to study the influence of chemical crosslinking on the recrystallization behavior of PVC. X_c and the melting temperature of crystallite (T_m) of PVC are shown in Table II.

It can be seen that X_c and T_m change no more with the increase of gel fraction at the same annealing conditions. Hjertberg et al.¹⁹ observed the increase of T_m for high crosslinked PVC and considered that chemical crosslinking would decrease the mobility of PVC chains. However, the conclusion from Table II seems to be that the effect of chemical crosslinking on the recrystallization process could be ignored for lightly crosslinked PVC-TPE. So physical crosslinking caused by microcrystallites still exists for lightly crosslinked PVC-TPE.

A Structure Model of Lightly Chemical Crosslinked PVC-TPE

Considering the above results and discussion, we proposed a structure model of lightly chemical crosslinked PVC-TPE as shown in Figure 3.

According to the proposed model, the chemical crosslinked PVC-TPE is composed of DEHP swollen microgel phase and sol phase. In the microgel phase, PVC chains are mainly crosslinked by chemical bonds, but the physical crosslinking caused by microcrystallites and chain entanglements also exists. In the sol phase, PVC chains are physically crosslinked by microcrystallites

Table III Effect of the Gel Fraction of PVC on the Processability Measured by the Torque Rheometer

Sample Code	Gel Fraction (%)	DP of sol	Gelation (Time/s)	Equilibrium (Torque/N m)	Equilibrium Melting Temperature (°C)
S1000	0	985	18	2.0	174
C9	24.4	1095	20	5.6	178
C14	32.0	1065	24	6.4	178
C5	55.5	1060	96	10.35	182

and entanglements. Some PVC sol chains may penetrate to the microgel and cocrystallize or entangle with gel chains, and thus connects the chemical crosslinking network of microgel phase and the physical crosslinking network of sol. Both physical network and chemical network contribute to the elasticity of chemical crosslinked PVC-TPE and act cooperatively. The elasticity contributed by physical crosslinking network is determined by the degree of crystallinity and molecular weight of sol (molecular weight has great effect on chain entanglements). The elasticity contributed by chemical crosslinking network is determined by the effective chemical crosslinking density.

The Rheological Property of Lightly Chemical Crosslinked PVC-TPE

The rheological property of PVC compound is characterized in two ways. First, the gelation property of plasticized PVC powders is deter-

mined by torque rheometer. Several parameters, such as the gelation time, equilibrium torque, and equilibrium melting temperature, are used to characterize the processability of PVC. Second, the rheological property of chemical crosslinked PVC-TPE is measured by capillary rheometer. The dependence of shear rate and apparent viscosity on the shear stress are obtained for different PVC compounds.

The results of torque rheometer measurements are shown in Table III. It can be seen that the gelation time, equilibrium torque, and equilibrium melting temperature of PVC-TPE increase as the gel fraction increases.

Figure 4 and Figure 5 show the influence of the gel fraction on the shear rate and apparent viscosity of PVC compounds at different shear stress, respectively. It can be seen that the shear rate decreases and apparent viscosity increases as the gel fraction increases. The apparent viscosity of chemical crosslinked PVC-TPE is much higher than that of uncrosslinked PVC.

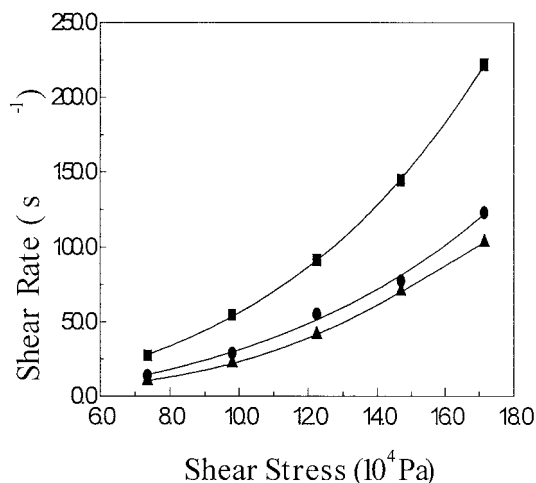


Figure 4 The relationship of shear stress and shear rate for different PVC-TPE at 184°C. ■: C9; ●: C4; ▲: C6.

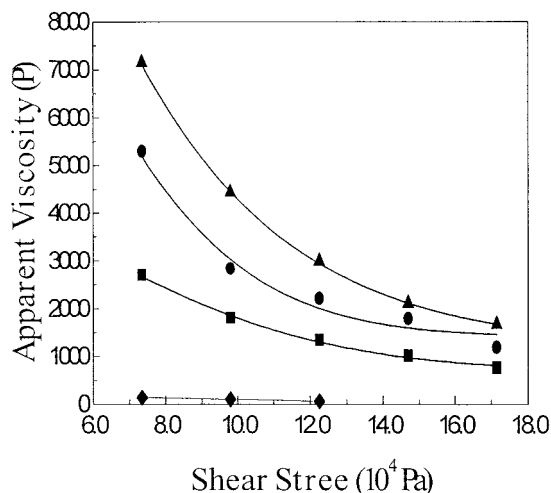


Figure 5 The relationship of shear stress and apparent viscosity for different PVC-TPE at 184°C. ■: C9; ●: C4; ▲: C6; ◆: S1000.

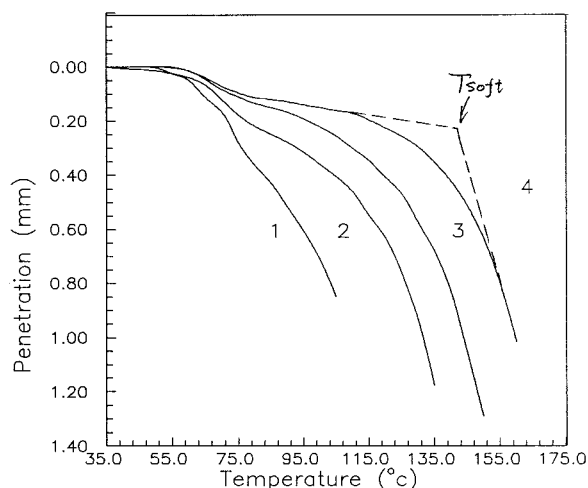


Figure 6 Effect of the gel fraction on the penetration-temperature curve of PVC-TPE. 1: S1000 ($w_g = 0$); 2: C9 ($w_g = 24.4\%$); 3: C4 ($w_g = 53.1\%$); 4: C6 ($w_g = 72.1\%$).

It may be concluded that chemical crosslinking has great influence on the rheology of PVC; PVC becomes more difficult to process as the gel fraction increases, but can still be reprocessed when the gel fraction of PVC is 72.1%.

Penetration Behavior of Chemical Crosslinked PVC-TPE

The penetration-temperature curve can reflect the deformation resistance of polymer material and be used to determine the elasticity and the maximum application temperature of material. The penetration-temperature curves for different PVC are shown in Figure 6. The “softening temperature” (T_{soft}) can be obtained from the experimental curves by plotting two slope lines as shown on one curve of Figure 6.

Figure 6 shows that the penetration value increases slowly with increasing temperature when temperature is lower than T_{soft} , and increases rapidly when temperature exceeds T_{soft} . T_{soft} can be used to determine the maximum application temperature of PVC. It also shows that the penetration value of uncrosslinked plasticized PVC (curve 1) is larger than that of chemical crosslinked PVC-TPE (curves 2, 3, 4) at the same temperature, and T_{soft} of uncrosslinked PVC is lower (about 90°C) than that of chemical crosslinked PVC-TPE. For crosslinked PVC, the penetration value decreases and T_{soft} increases as the gel fraction increases.

It is generally accepted that PVC resin and plasticized PVC contain small crystallites and that a physical crosslinking network can be formed by these crystallites. Plasticized PVC exhibits somewhat rubber-like elasticity and deformation resistance over a certain temperature range due to the presence of the physical crosslinking network. PVC crystallites begin to melt at 90°C and physical crosslinking network is destroyed progressively. So uncrosslinked plasticized PVC shows a larger penetration value under stress above 90°C. According to the structure model of chemical crosslinked PVC-TPE, the elasticity is contributed by two networks: physical crosslinking network and chemical crosslinking network. Since chemical network is more stable than physical network at high temperature, then chemical crosslinked PVC-TPE exhibits smaller penetration value and higher softening temperature than uncrosslinked PVC.

The Elasticity of Chemical Crosslinked PVC-TPE

The elasticity of PVC-TPE can be judged by its permanent compression set value in some way. The lower the permanent compression set value, the better the elasticity is. Table IV presents the dependence of permanent compression set on the structure of PVC.

From Table IV, it can be seen that the permanent compression set decreases as the DP of sol and the gel fraction increase. The elasticity of chemical crosslinked PVC-TPE is contributed by the physical and chemical crosslinking networks, so DP of sol and the gel fraction affect the compression set of PVC simultaneously. It is concluded that chemical crosslinked PVC-TPE exhibits better elasticity than common flexible PVC.

Table IV Effects of Structure Factors on the Permanent Compression Set of PVC-TPE

Sample Code	Gel Fraction (%)	DP of sol	Permanent Compression Set (%)
C0	0	1732	64.2
C1	8.7	2790	54.6
C9	24.4	1095	60.6
C10	30.1	800	58.7
C2	32.7	1634	56.8
C11	50.9	679	55.0
C4	53.1	1038	54.2
C6	72.1	656	52.1

CONCLUSION

Lightly chemically crosslinked PVC was prepared by VC/DAP suspension copolymerization. The gel fraction, DP of sol, and the crosslinking density of gel are influenced by the feed concentration of DAP and polymerization temperature. PVC prepared by VC/DAP copolymerization was lightly crosslinked. Physical entanglements had great influence on the crosslinking density of gel when the gel fraction was high. Chemical crosslinking had little effect on the recrystallization of PVC-TPE. A physical model of lightly chemical crosslinked PVC-TPE was proposed, in which chemical networks were acted cooperatively with physical networks. The processability of PVC-TPE deteriorated with chemical crosslinking, but the dimensional stability and the maximum application temperature were raised by chemical crosslinking. The gel fraction and DP of sol influenced the permanent compression set of chemical crosslinked PVC-TPE simultaneously and interpreted by the present structure model.

REFERENCES

1. Brown, H. R.; Musindi, G. M.; Stachuski, Z. H. *Polymer* 1982, 23, 1508.
2. Ballard, D. G. H.; Burgess, A. N.; Dekoninck, J. M.; Roberts, E. A. *Polymer* 1987, 28, 3.
3. Obande, O. P.; Gilbert, M. *J Appl Polym Sci* 1989, 37, 1713.
4. Nethsinghe, L. P.; Gilbert, M. *Polymer* 1988, 29, 1935.
5. Browner, T. N.; Davis, D. D.; Kwei, T. K.; Vroom, W. I. *J Appl Polym Sci* 1983, 28, 3527.
6. Behal, M. *J Appl Polym Sci* 1989, 37, 429.
7. Hjertberg, T.; Dahl, R.; Sorvik, E. *J Appl Polym Sci* 1989, 37, 1239.
8. Mori, K.; Nakamura, Y. *J Macromol Sci Chem Eds* 1978, A22(2), 209.
9. Mori, K.; Nakamura, Y. *J Appl Polym Sci* 1978, 22, 2685.
10. Itoh, I.; Itoh, S.; Matsumura, I.; Maruyama, H. *J Polym Sci Part C* 1971, 33, 135.
11. Jpn. Kokai Koho Patent, JP 59-43045, JP57-111341, JP58-47011.
12. Flory, P. J. *J Chem Phys* 1950, 18, 108.
13. Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook, 2nd ed.; Wiley-Interscience: New York, 1975; Vol IV, p 132.
14. Bao, Y.; Weng, Z.; Huang, Z.; Pan, Z. *Int Polym Process* 1996, 11(4), 369.
15. Anagnostopoulos, C. E.; Coran, A. Y. *J Appl Polym Sci* 1960, 4, 181.
16. Patterson, K. G.; Padgett, S. J.; Peppas, N. *Colloid Polym Sci* 1982, 260(9), 851.
17. Langley, N. R.; Polmanteer, K. E. *J Polym Sci Polym Phys Ed* 1974, 12, 1203.
18. Flory, P. J. *Chem Rev* 1944, 35, 51.
19. Hjertberg, T.; Dahl, R. *J Appl Polym Sci* 1991, 42, 107.