

Poly(vinyl acetate)/Polyacrylate Semi-interpenetrating Polymer Networks, Part 1: Synthesis and Polymerization Kinetics

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ABSTRACT: Bulk photopolymerization was used to synthesize a series of semi-interpenetrating polymer network (s-IPN) based on linear poly(vinyl acetate) and crosslinked *N*-butyl acrylate/1,6-hexandiol diacrylate (HDDA) copolymer. Different formulations were used by varying the monoacrylate/diacrylate molar ratio and the linear polymer concentration. The polymerization kinetics was studied as a function of the s-IPN composition by FTIR spectroscopy. It was observed that the reaction rate increases by increasing the linear polymer amount. This effect is much more pronounced in the reaction mixtures

with a higher diacrylate concentration, playing a key role the restricted mobility of the macroradicals involved in the bimolecular termination. The maximum conversion increases regularly with linear polymer concentration in the blend and resulted to be very high, ranging from 95 to 98%. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2669–2674, 2009

Key words: semi-interpenetrating networks (s-IPN); photopolymerization; polymerization kinetics; polyacrylate; poly(vinyl acetate)

INTRODUCTION

Ultraviolet (UV)-induced polymerization allows the transformation of liquid monomer into solid polymer through a very fast reaction. It is the most effective way to transform a solvent-free liquid resin into a solid polymer at room temperature. Most important applications of such technique are found in the coating industry, namely varnishes, paints, and printing inks. Because of their rapid and extensive polymerization, mono- or polyfunctional acrylic monomers were photopolymerized to obtain transparent films. Their chemical, physical, mechanical, and morphological properties may be directed by means of the appropriate choice of reactants, chemical composition, and crosslinking degree.^{1,2} Otherwise, to give peculiar properties to the resin, multicomponent system may be prepared by copolymerization^{3,4} blending or interpenetrating (IPN)⁵ or semi-interpenetrating (s-IPN)⁶ polymer network formation, obtained by the acrylate tridimensional network synthesis in presence of a linear polymer.

In s-IPN the phase separation degree and the morphology are controlled by the progressive segregation of the linear polymer from the growing network, which is in turn influenced by the diffusion restrictions imposed by the network formation. Both the processes depend on s-IPN composition, i.e., crosslinker multifunctional monomer and linear polymer concentration.

In this article we report the synthesis of semi-interpenetrating polymer networks (s-IPNs) constituted by *n*-butyl acrylate (BA) and 1,6-hexandiol diacrylate (HDDA), in the presence of poly(vinyl acetate) (PVAc), dissolved in the monomer mixture. The influence on double bonds conversion kinetics, studied by FTIR spectroscopy, was investigated as a function of the s-IPN composition. It was observed that both the crosslinker (HDDA) concentration and the PVAc content control the polymerization rate as well as the chemical, physical, mechanical, and morphological properties of the IPNs, as it will be reported in a forthcoming paper.

EXPERIMENTAL

Sample preparation

s-IPNs, based on crosslinked acrylate and linear PVAc, were synthesized in bulk by photopolymerization. Two series of s-IPNs with different

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TABLE I
Semi-interpenetrating Polymer Network Name and Formulation

s-IPN series	Sample name	BA (wt %)	HDDA (wt %)	BA/HDDA (mol/mol)	PVAc (wt %)
s-IPN-A	A0	50	50	1.8	0
	A9	45.5	45.5	1.8	9.0
	A17	41.6	41.6	1.8	16.8
	A23	38.5	38.5	1.8	23.0
	A28	35.8	35.8	1.8	28.4
s-IPN-B	B0	70	30	4.1	0
	B9	63.7	27.3	4.1	9
	B17	58.4	24.8	4.1	16.8
	B23	53.8	23.2	4.1	23.0
	B28	50.2	21.4	4.1	28.4

crosslinking density were prepared by reacting BA (Aldrich) and HDDA (Aldrich, St. Louis, MO) (crosslinker) in molar ratios BA/HDDA 1.8 : 1 (s-IPN-A) and 4.1 : 1 (s-IPN B) in the presence of different PVAc amount (0–28.4 wt %). The average molar mass of PVAc (Aldrich, St. Louis, MO) is 167,000 and its glass temperature is in the range between 17 and 32°C. PVAc was added in the liquid acrylate monomers and the dissolution was obtained within 10 h at room temperature. Then, 2 wt % of photoinitiator 2-hydroxy-2-methyl-1-phenyl propanone (Darocur 1173, Ciba, Basel, Switzerland) was added under stirring during 1 h in the absence of light to avoid the reaction beginning. The different s-IPN's formulations and sample names are given on Table I.

Samples were photopolymerized at room temperature. A drop of the reaction liquid mixture was deposited between two NaCl dishes to minimize the oxygen diffusion. The thickness of the curable film was so as to ensure a peak intensity at 1725 cm⁻¹ between 0.8 and 1.2 absorbance units in the FTIR spectra (about 10 μm). Two medium pressure mercury lamps with the irradiation wavelength at 305 nm were used as irradiation source. The light intensity was 0.32 mW/cm², as measured by radiometry (UV Integrator, Primarc UV Technology, Slough, UK). The curing was carried out in air by irradiating one sample side for various irradiation time *t*.

Infrared spectroscopy

After having subjected the samples to different irradiation doses, Fourier transform infrared (FTIR) spectra were recorded with a Perkin–Elmer 2000 (Waltham, MA) coadding 32 scans at 2 cm⁻¹ resolution. The spectra were acquired in the absorbance mode. After a proper baseline correction between 787 and 833 cm⁻¹, the intensity decrease of the peak at 817 cm⁻¹, corresponding to the H₂C=CH out-of-plane deformation of the acrylate double bonds, was used to follow the polymerization kinetics. The

degree of conversion *p* was calculated at a given irradiation exposure by using the formula:

$$p = 1 - \frac{(A_{\lambda}/A_{\lambda 0})_t}{(A_{\lambda}/A_{\lambda 0})_{t=0}} \quad (1)$$

where $(A_{\lambda})_{t=0}$ is the initial absorbance value at the chosen frequency and $(A_{\lambda})_t$ is the absorbance value after a total irradiation time *t*. To take into account the possible sample thickness change during the polymerization, the sample spectrum was normalized respect to the reference peak intensity at 1725 cm⁻¹ (λ_0), assigned to C=O stretching (baseline correction between 1670 and 1790 cm⁻¹).

The *p* slope versus the irradiation time *t* is proportional to the polymerization rate R_p , which can be calculated as

$$R_p = \frac{dp}{dt} \quad (2)$$

Actually, in this study, *p* and R_p are apparent quantity, in that in our measurements it was taken into account the polymer formation during the UV irradiation as well as in the subsequent period to the FTIR acquisition completion (dark polymerization). This may bring about an overestimation of *p* values.⁶

The reported conversion degree and polymerization rate data are the mean values calculated from at least four independent experiments.

RESULTS AND DISCUSSION

The photoinitiator absorbs the incident light and readily generates reactive radicals (radical polymerization). The monoacrylate (BA) and difunctional acrylate (HDDA) monomers, upon polymerization, will constitute the backbone of the three-dimensional polymer network.

Figure 1 shows a typical FTIR spectrum of the mixture BA/HDDA (4.1/1) with the two absorption

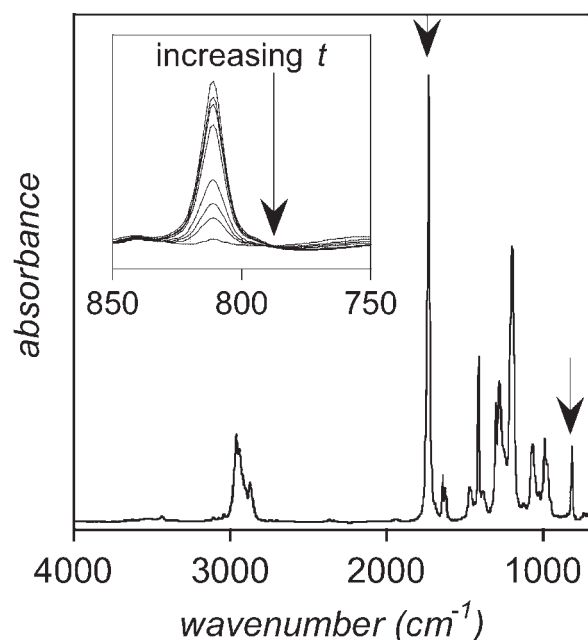


Figure 1 FTIR spectrum of BA/HDDA 4.1/1 mixture before irradiation. In the inset is reported the evolution of 810 cm^{-1} peak with the irradiation time (t) increase.

peaks (817 and 1725 cm^{-1}) indicated by an arrow, which were used to calculate the conversion degree. The intensity decrease of the $\text{H}_2\text{C}=\text{CH}$ absorption peak with the increase of the irradiation time t is shown in the inset of Figure 1.

The eqs. (1) and (2) permit to calculate the conversion degree p of the $\text{C}=\text{C}$ groups and their reaction rate R_p . To study the influence of the crosslinker concentration and the linear polymer content in the s-IPNs on the photocuring reaction, the initial and the maximum reaction rates (R_i and R_{\max}), the conversion at the first and second gel point (p_{gel1} , p_{gel2}), and its maximum value (p_{\max}) were determined as indicated in Figure 2, where the conversion and the polymerization rate of A17 sample is reported as a function of the irradiation time t .

In Figure 3 the kinetic profiles of the polymerization of s-IPN-a and s-IPN-B are displayed.

In general, it may be observed that from the early polymerization stage the conversion rate from the initial value R_i slows down before reaching the conversion p_{gel1} . This effect is more evident in the samples with the higher HDDDA concentration (s-IPN-A).

The R_i value is proportional to the initial overall concentration of both BA and HDDDA double bonds. In fact, as shown in Figure 4, where R_i was reported as a function of the $\text{C}=\text{C}$ concentration expressed in mole per gram of reaction mixture, it does not depend on the molar ratio of the two monomers. In this case the PVAc does not directly influence the reaction rate, acting just as diluent.

As the conversion increases, the polymerization proceeds via gel effect: the viscosity of the system reaches a critical value at which the bimolecular termination is controlled by the restricted macroradical diffusion. The conversion at which this process takes place, p_{gel} (see Fig. 2), strongly depends on the HDDDA concentration, which controls the crosslinking density, and on the PVAc content, which contributes to the reaction mixture viscosity (Fig. 5).

The higher is the HDDDA concentration or the PVAc content, the lower is the p_{gel} .

Above p_{gel} the polymerization rate rapidly increases reaching its maximum value R_{\max} , reported in Figure 6 as a function of PVAc content.

At this polymerization stage, it may be observed that R_{\max} increases with increasing PVAc amount in the blends and that the series A samples react systematically faster than those of the series B. To interpret these experimental results, various phenomena which occur simultaneously may be invoked.

The increase of the PVAc amount, and hence the decreases of the double bond concentration, should have opposite effect on the reaction rate. As it may be supposed, the reacting blend viscosity increase with the linear polymer concentration should be the prevailing factor affecting the polymerization kinetics. The diffusion of the growing chains becomes more difficult, and thus the termination reaction could be prevented, while the monomer

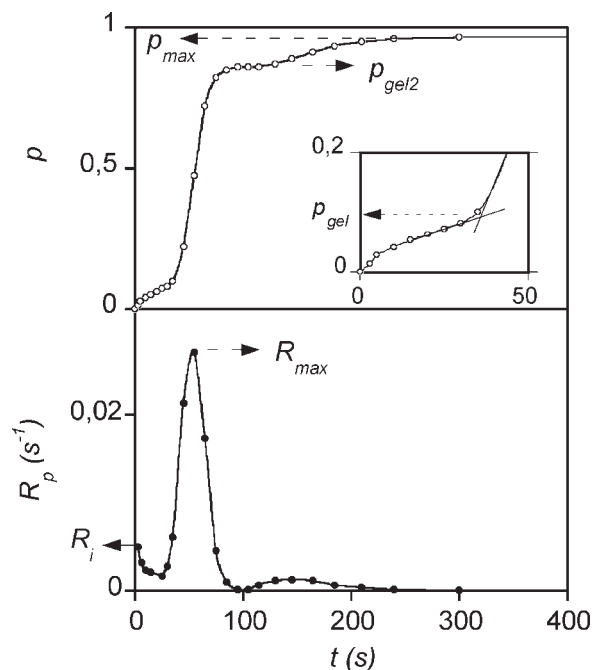


Figure 2 Double bond conversion and polymerization rate versus irradiation time t for A17 sample. The kinetic parameters p_{gel1} , p_{gel2} , p_{\max} , R_i , and R_{\max} (see the text) are indicated.

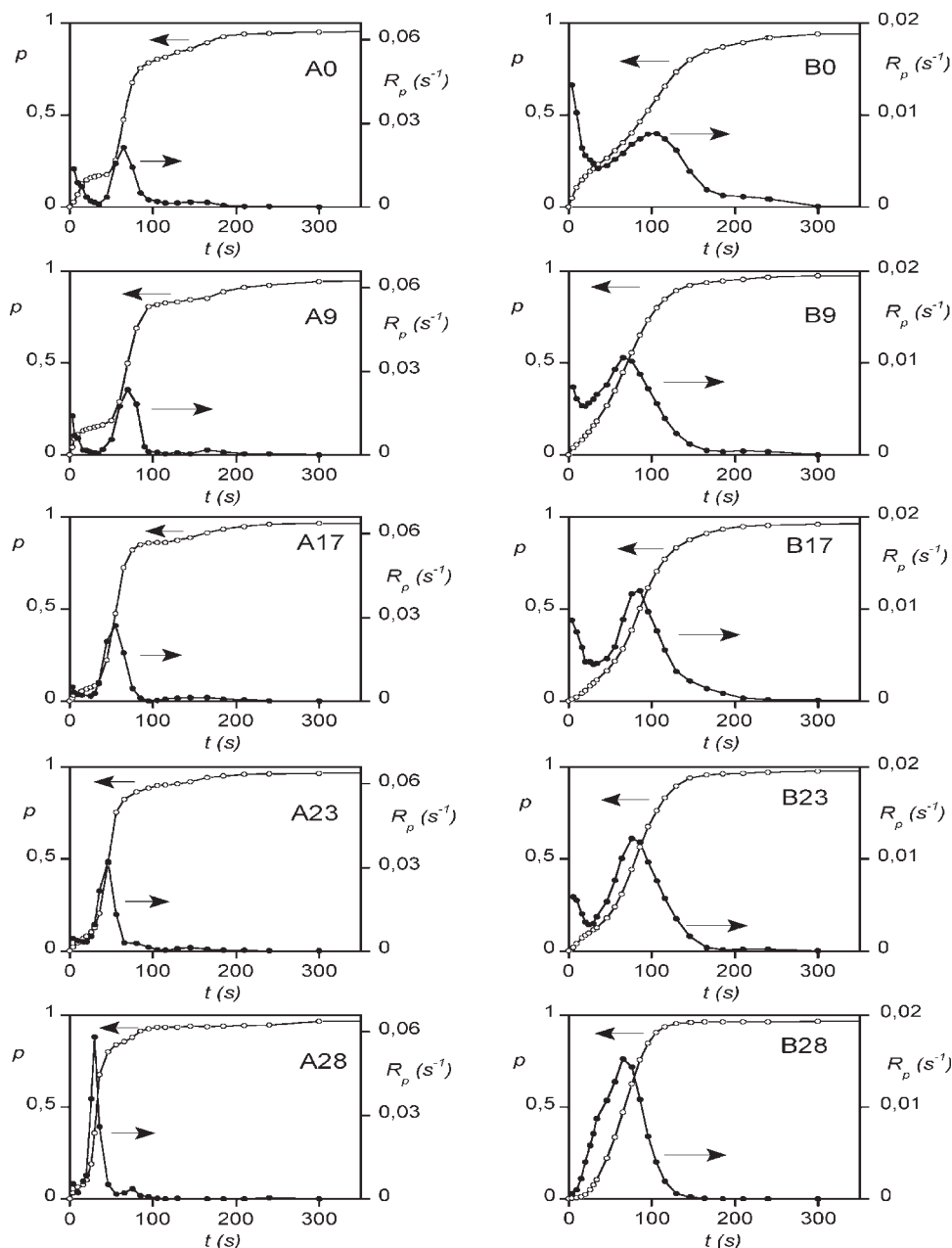


Figure 3 Double bond conversion and polymerization rate of s-IPN-A and s-IPN-B as a function of irradiation time. See Table I for the sample names and formulations.

diffusion remains high because of its small size. Hence, the macromolecular chains continue to grow and the polymerization rate increases.

Moreover, it is well known that the oxygen reacts with the free radicals to form peroxide radicals which are not reactive.⁷ Although the transport of oxygen into the polymerizing sample between the two NaCl dishes should be minimal, the presence of PVAc could slow down the oxygen diffusion in the blend films and thus the free radical deactivation.¹ A strong influence of PVAc on the polymerization is confirmed by the fact that we could not obtain solid

films of pure acrylates in air without using the two NaCl windows.

These considerations cannot alone explain the results of Figure 6.

For sure, it can be excluded that the differences between the polymerization rate of the blends A and B are due to a higher HDDDA reactivity respect to that of the BA monomer. In fact, a significantly different behavior should have had affected in the early polymerization stage, when the kinetics is controlled by the monomers reactivity. As shown in Figure 4, this is not the case.

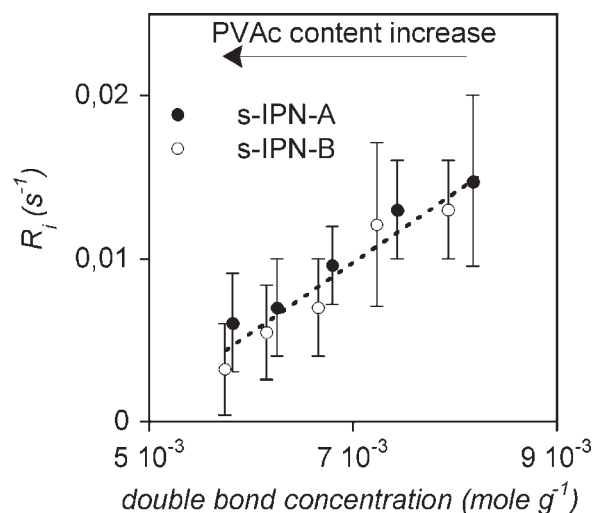


Figure 4 Dependence of the initial reaction rate R_i on the double bond concentration.

Hence, the different behavior of the two sample sets is to be ascribed to the different crosslink density.

In s-IPNs physicochemical and morphological characterization experiments (data not yet published), we observed that the more densely crosslinked s-IPN-A acrylate network does not show any glass transition and that it can incorporate PVAc in its smaller meshes, partially hampering its segregation. In this case, the viscosity increases and the autoacceleration effect is intensified by the presence of the linear polymer. On the other hand, s-IPN-B shows the crosslinked acrylate glass transition at about -7°C , well below the polymerization temperature, as well as a segregated structure. This

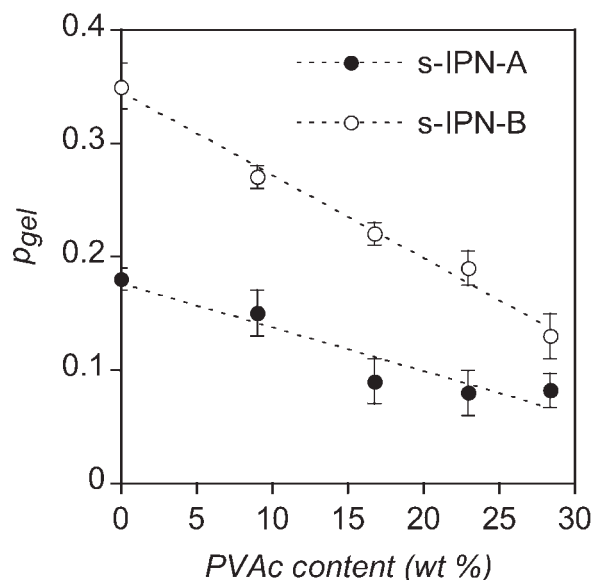


Figure 5 Dependence of the gel point conversion p_{gel} on PVAc content in s-IPN-A and s-IPN-B samples.

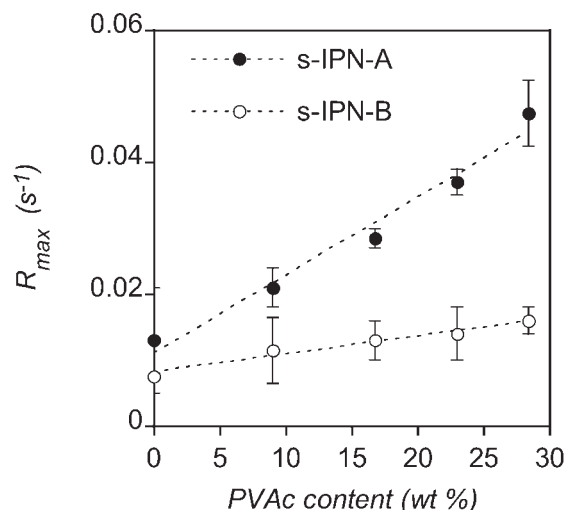


Figure 6 Dependence of the maximum polymerization rate R_{max} on PVAc content in s-IPN-A and s-IPN-B samples.

phenomena contribute to an acrylate polymer higher mobility, presumably less affected by PVAc content, and hence to a minor autoacceleration effect.

At the higher conversion the polymerization rate decreases because of the slowing down of the monomer diffusion. In some experiments, mainly referred to s-IPN-A samples, before the final maximum conversion attainment, a second gel point may be observed at about $p_{gel2} = 0.85$ (Figs. 2 and 3). In Figure 7 the maximum conversion values (p_{max}), all measured after an irradiation time of 900 s, are reported as a function of PVAc content in the two s-IPNs.

It increases regularly with the linear polymer concentration in the blend.

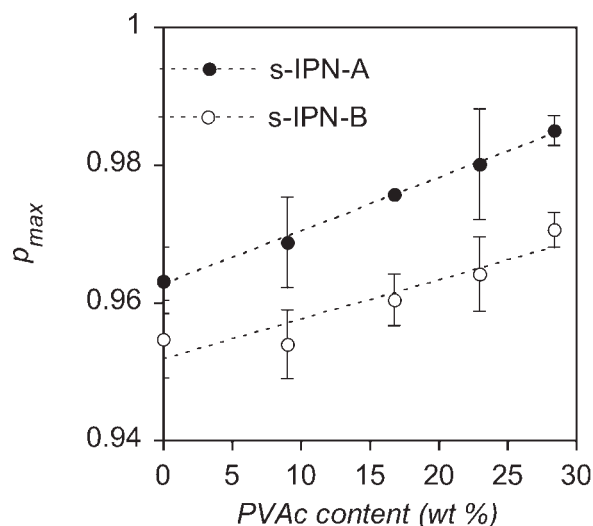


Figure 7 Dependence of the maximum conversion p_{max} on PVAc content in s-IPN-A and s-IPN-B samples.

Despite the tight network formation and the linear polymer insolubilization, the photopolymerization resulted to be an effective method for the preparation of highly crosslinked s-IPN network from a system endowed with a very low mobility.

The polymerization was rapid and quantitative and the obtained transparent films are characterized by interesting mechanical properties exploitable in coating applications, as will be shown in a forthcoming paper.

CONCLUSIONS

The bulk photopolymerization kinetics of mono and diacrylate monomers in the presence of PVAc was followed by means of FTIR spectroscopy. The conversion and polymerization rate were recorded in a wide composition range, obtained by varying the monomer molar ratio and the PVAc concentration.

The higher is the linear polymer amount, the lower is the conversion at the gel point.

The maximum polymerization rate increases with increasing PVAc content. This effect is amplified by high diacrylate monomer concentration.

The maximum conversion increases regularly with linear polymer content in the blend, reaching values between 95 and 98%.

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References

1. Andrzejewska, E.; Andrzejewska, M. *J Polym Sci Part A: Polym Chem* 1998, 36, 665.
2. Lacamp, L.; Youssef, B.; Bunel, C.; Lebaudy, P. *Polymer* 1997, 38, 6069.
3. Dubé, M. C.; Penlidis, A. *Polymer* 1995, 36, 587.
4. Chu, H.-H.; Lee, C.-H.; Huang, W. G. *J Appl Polym Sci* 2004, 91, 1396.
5. Duenas, J. M.; Escuriola, D. T.; Ferrer, G. G.; Pradas, M. M.; Ribelles, J. L. G.; Pissis, P.; Kyristis, A. *Macromolecules* 2001, 34, 5525.
6. Moussa, K.; Decker, C. *J Polym Sci Part A: Polym Chem* 1993, 31, 2633.
7. Moussa, K.; Decker, C. *J Appl Polym Sci* 1987, 34, 1603.