Transesterification and Crosslinking of Poly(vinyl chlorideco-vinyl acetate) Copolymers in the Melt

M. ANASAGASTI,¹ M. HIDALGO,² C. MIJANGOS²

¹ Departamento de Química-Física, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48048 Lejona (Vizcaya), Spain

² Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

Received 12 March 1998; accepted 3 August 1998

ABSTRACT: A new method to obtain hydroxylated poly(vinyl chloride) (PVC-OH) and its crosslinking in the melt are studied. Starting from a vinyl chloride-co-vinyl acetate copolymer, a transesterification reaction in the presence of an alcohol during the processing of plasticized polymer is investigated as a function of the processing temperature and alcohol nature (1-butanol or 1-octanol). Reaction evolution is followed by ¹H-NMR and IR spectroscopies. The best results are obtained for 1-octanol, and they show the absence of secondary reactions and the progressive appearance of OH groups in the polymer as acetate groups disappear. On the other hand, crosslinking of the thus-obtained PVC-OH with hexamethylene diisocyanate (HMDI) during the processing is also studied. The gel content and the mechanical properties at 140°C are studied as a function of three crosslinking variables: number of OH groups present in the polymer, concentration of HMDI added to the polymer, and time of crosslinking. The results show that by optimizing those parameters it is possible to obtain gel contents up to 100% and an increase of 600% in the Young's modulus and 1300% in the ultimate tensile strength with respect to the plasticized PVC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 621-630, 1999

Key words: vinyl chloride–vinyl acetate copolymer; transesterification reaction; hydroxylated poly(vinyl chloride); crosslinking; reactive processing

INTRODUCTION

The four commodity polymers, polyethylene, poly-(vinyl chloride), polypropylene, and polystyrene, represent the biggest world market share of polymers, about 75%. Their production is increasing year by year, due, on the one hand, to the new markets emerging in South America and East Asia and, on the other, to the new derivatives of these polymers that provide greater or new properties, and, therefore, which are suitable for a greater number of applications.

Nowadays, there is a large number of new structures for each of these commodity polymers, coming either from the fabrication process, that is, by copolymerization with other monomers, or from the transformation process, that is, reactive extrusion. Polymers of a hydrocarbon nature are of relatively poor chemical reactivity, for which the grafting of polar groups or comonomers in the chain is demanded. Examples of polymer modification of polyethylene and polypropylene with acrylic acid, organosilane derivates, maleate, and maleic acid and others have been widely reported in the literature.^{1–5}

Correspondence to: C. Mijangos.

Contract grant sponsor: Comision Interministerial de Ciencia y Tecnología (CICYT); contract grant number: MAT96-0615.

Journal of Applied Polymer Science, Vol. 72, 621-630 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/050621-10

The controlled incorporation of a hydroxyl, acid, or amine group in a polymer is the most preferred among the different reactive groups. Modification/substitution reactions of polymers under industrial conditions have been investigated from two points of view: One by developing continuous equipment (extruders), that is, incorporating multiple injection points, sealed vent chambers, solvent-recovery systems, etc. The other is by fundamental studies of the chemical reactivity of these polymers in the melt. There are few laboratories devoted to basic studies of the reactivity of polyethylene, polypropylene, poly-(ethylene-vinyl acetate), and poly(vinyl chloride) (PVC) with different reagents and monomers in the melt and its correlation with solution reactions. $^{5-10}$

In this regard, Lambla et al.¹¹ demonstrated the feasibility of a transesterification reaction of the ethylene—vinyl acetate copolymer with a variety of alcohols in solution and discontinuous and continuous melts.

In our lab,^{12–15} we demonstrated the feasibility of the substitution reaction on PVC with a large amount of thiolate derivatives in solution and discontinuous and continuous melts. Although we have prepared hydroxylated PVC in solution,^{16,17} until this work, we have not obtained a PVC-OH polymer under industrial conditions, in spite of the potential applications (compatibility and adhesion with other polymers or materials, grafting of additives, etc.). This work refers to the alcoholysis of a poly(vinyl chloride–vinyl acetate) [P(VC– VAc)] copolymer and its ulterior crosslinking during reactive processing.

EXPERIMENTAL

Materials

The polymer was a commercial emulsion polymerized poly(vinyl chloride-*co*-vinyl acetate) [P(VC*co*-VAc)] copolymer (ETINOX 400) from Aiscondel Industries (Spain), with a 5% molar content in vinyl acetate. 1-Octanol, 1-butanol, dibutyltin dilaurate (DBTDL), and dibutyltin oxide (DBTO) were commercial products from Fluka, and dioctylphthalate (DOP), from Jaber. The crosslinking agent, 1,6-hexamethylene diisocyanate (HMDI), was obtained from Aldrich.

Reactive Processing (Transesterification)

The transesterification reactions in the melt were carried out in a Haake Rheocord 9000 unit cou-

Table I	Transesterification Reaction: Reactiv	es
and Proc	essing Conditions Employed	

Run	Alcohol	Catalyst	Temperature (°C)	Processing Time (min)
1	_	_	140	25
2			160	25
3	1-Butanol	_	140	25
4	1-Butanol	_	160	25
5	1-Butanol	DBTDL	140	30
6	1-Butanol	DBTDL	160	30
$\overline{7}$	1-Octanol	_	160	20
8	1-Octanol	DBTO	140	50
9	1-Octanol	DBTO	150	45
10	1-Octanol	DBTO	160	40
11	1-Octanol	DBTO	170	30
12	HMDI	_	160	40

pled to a Rheomix 600 mixer with rolling rotors. Four components were premixed to obtain a homogeneous initial mixture: polymer, catalyst, plasticizer (DOP), and alcohol. The premixed compound was then introduced into the mixer at the selected temperature and rotor shear rate.

The temperature and reaction time were varied to observe their influence on the reaction, but the rotor shear rate was kept constant at 40 rpm, and the DOP concentration was 20 phr in all experiments. The ratio of VAc/alcohol was also kept constant and equal to 1. The catalyst, DBTDL or DBTO, was added to the initial premixture in a concentration of 1 phr.

Kinetic evolution was followed by withdrawing samples at progressively increasing reaction times. Samples were purified twice by dissolving in THF and precipitation with methanol. Rheological evolution was followed via torque registration. Table I shows the reaction conditions for the different transesterification reactions carried out.

Degree of Modification

The transesterification reaction was followed by IR spectrophotometry using the evolution of the ratio $I(1740 \text{ cm}^{-1})/I(1428 \text{ cm}^{-1})$, that is, $I(\nu C = O)/I(\nu C H_2)$, with the reaction time. In addition, the evolution of the transesterification reaction was followed by ¹H-NMR spectroscopy of the modified polymer solutions in deuterated dioxane, using a Varian Gemini 200-MHz spectrometer with a 90° pulse at room temperature.

Crosslinking Reaction

The crosslinking of the poly(vinyl chloride-vinyl acetate-vinyl alcohol) [P(VC-VAc-VA)] terpoly-

Run	[NCO]/[[OH] ^a	$t_{ m processing}^{\ \ b} \ ({ m min})$	$t_{ m crosslinking}^{ m c}$ (min)
13	1	4	0.5
14	1	7.5	0.5
15	1	15	0.5
16	1	7.5	1
17	1	7.5	2
18	0.3	15	0.5
19	0.5	15	0.5
20	1	15	1

Table IICrosslinking Conditions Employedwith Run 11

 $^{\rm a}$ [NCO] = 2 [HMDI]; [OH] is the maximum possible concentration of OH groups in the polymer, that is, 5% molar.

^b $t_{\text{processing}}$ is the time of processing for the transesterification reaction.

 $^{\rm c}\,t_{\rm crosslinking}$ is the time of processing after the crosslinking agent addition.

mers obtained by reactive processing—using run 11 in Table I—was carried out by adding the crosslinking agent (HMDI) to the molten polymer during the processing at 170°C and for different reaction times. The crosslinking time, that is, the processing time after the crosslinking agent addition, was also varied. Different ratios of HMDI, with respect to the theoretical maximum number of OH groups present in the polymer, were employed. After processing, the melted polymer was molded in sheets in a laboratory press for 2 min at 50 bar and 170°C, followed by cooling for 1 min at 50 bar and 15°C. Table II shows the reaction conditions for the different crosslinking reactions studied.

Gel Content

The gel content, expressed in percent, was determined by Soxhlet extraction of the crosslinked samples, using tetrahydrofurane as the solvent, applying eq. (1), where w_f corresponds to the sample weight after extraction, and w_0 , the weight of the polymer in the whole weight of the initial sample before extraction (determined from the sample composition):

$$\% \text{ Gel} = \frac{w_f}{w_0} \times 100 \tag{1}$$

Mechanical Properties

Study of the mechanical properties was carried out from the stress-strain curves obtained in an Instron 4031 universal testing machine. Measurements were carried out using a 0.1 kN load cell, with a testing speed of 50 mm/min, at 140°C, employing dumbbell-shaped test samples cut from crosslinked polymer sheets.

RESULTS AND DISCUSSION

On the basis of previous works with EVA,¹¹ different experiments were carried out as a function of the chemical nature of the alcohol employed, the chain length and first or second character in the OH group, and the catalyst. The transesterification reaction of the VC-*co*-VAc copolymer was studied as a function of temperature and reaction time.

Furthermore, the crosslinking of modified copolymers with diisocyanates was followed by means of the gel content determination using different variables such as the crosslinking agent concentration, the crosslinking time, and the concentration of OH groups present in the polymer (expressed as a function of the transesterification reaction time). The mechanical properties of the crosslinked polymers obtained were evaluated at temperatures above the T_g as a function of these three variables and compared to that of the unmodified copolymer.

Processing Under Different Conditions

Some explorative tests were carried out to evaluate the influence of the kind of alcohol and catalyst in the processing of the polymer. In Figure 1 are plotted rheograms of the plasticized polymer processed in the presence of butanol, octanol, and octanol and the catalyst. It is observed, first, that for the polymer processed in the presence of alcohol the value of the torque decreases, as expected, for a liquid substance added to the mixture. On the other hand, the rheograms show that, for the same amount of alcohol, the torque value is lower for octanol than for butanol, which is due to the lower boiling point of the butanol (116-118°C), which is evaporated during the processing, in comparison to that of octanol (193°C) and to the plasticizer character of 1-octanol. From the point of view of the processing, there is not a big difference for the mixture of the polymer, plasticizer, and alcohol with or without a catalyst, although the last is necessary for the alcoholysis of the polymer to occur, as described below.



Figure 1 Rheograms at 160°C and 40 rpm for different mixtures: (●) VC-*co*-VAc + DOP; (▲) VC-*co*- Vac + DOP + 1-butanol; (●) VC-*co*-VAc + DOP + 1-octanol; (■) VC-*co*-VAc + DOP + 1-octanol + DBTO.

Temperature Influence

Figure 2 shows rheograms for the P(VC-co-VAc) copolymer processed in the presence of the plasticizer, alcohol, and catalyst at different temperatures. In all the rheograms, the existence of a peak corresponding to the gelification/fusion process and stabilization in the torque value from 5 to 40 min is observed, except in the case of the processing at 170°C, which shows increase of this parameter due to the crosslinking of the polymer after 25 min.

On the other hand, as pointed out later, a higher rate in the alcoholysis reaction is obtained as the processing temperature increases. In conclusion, this part of the study shows that it is possible to process the polymer for 25 min until 170°C without any other secondary reaction than alcoholysis.

Alcoholysis of the VC-co-VAc Copolymer

The reaction of the polymer with the alcohol to give a VC–VAc–VA terpolymer or a VC-co-VA copolymer (named PVC-OH), as is indicated in Scheme 1, was followed by IR and ¹H-NMR spectroscopy. The progress of the reaction inside the processing chamber was followed by the extraction of samples at different time intervals and isolation of the polymer from the mixture by purification. No crosslinking was observed in the modified polymers.

The best way to evaluate the degree of modification is to follow, by ¹H-NMR, the decrease in the methyl groups as the acetate group is substituted by the hydroxyl group. In Figure 3 is plotted, as an example, the ¹H-NMR spectra of samples taken at 20 and 40 min of run 9 together with the original polymer.

Although quantitative results are not very accurate from these spectra, because of the low content of acetate groups in the polymer, qualitative differences are easily appreciated in the original figures. Thus, it is seen that the band at 5.3 ppm, which corresponds to the VAc proton, CH_2 —CH—OOC— CH_3 , decreases with time. The same evolution is observed in the overlapped band at 2.05 ppm, which corresponds to the methyl protons in the same group as above. These results show indirectly that the reaction of alcoholysis for the VC–VAc copolymer, that is, the apparition of OH groups, takes place during normal processing conditions for the polymer.

The kinetics of the alcoholysis can be studied by IR spectra. In Figure 4, given as an example, are some spectra of the modified polymer for different processing times in run 10 and the original polymer. In this figure it can be observed that the original polymer exhibits a specific band at 1740 cm⁻¹ which corresponds to the acetate group and



Figure 2 Rheograms of VC-*co*-VAc + DOP + 1-octanol + DBTO mixture at 40 rpm and different temperatures: (**I**) 140°C; (\blacklozenge) 150°C; (\blacklozenge) 160°C; (\blacktriangle) 170°C.



Scheme 1

that this band disappears as time progresses. Simultaneously, in the spectra, the appearance of a new band at $\approx 3300~{\rm cm^{-1}}$ is observed, corresponding to the OH groups formed during the alcoholysis reaction.

The band at 1428 cm⁻¹, which corresponds to CH_2 groups, does not practically vary, which allows it to be taken as a reference. No other appreciable differences are seen in the spectra.

In Figure 5 are plotted the intensity ratio of the $1740/1428 \text{ cm}^{-1}$ bands for different conditions of the reaction. In comparing curves 1, 2, 3, and 4, it is deduced first that the alcoholysis reaction starts for each temperature from the beginning of the processing and decreases with the time. Sec-



Figure 3 Evolution with processing time of ¹H-NMR spectrum of VC-*co*-VAc processed in the presence of DOP + 1-octanol + DBTO at 40 rpm and 150°C (run 9): (a) initial; (b) at 20 min; (c) at 40 min.

ond, as the temperature of the processing is increased, the rate of the alcoholysis reaction is higher. Third, for the reaction at 170°C for about 10 min, the acetate vinyl groups are transformed in an appreciable amount to OH vinyl groups, susceptible to crosslinking in a quantitative way as we will see in the next paragraph. For this run, at 25 min, the extent of the reaction is similar to that reached in about 40 min at 160°C, which is almost complete as was shown by NMR.

Crosslinking

Of interest in producing PVC-OH is that this polymer has a very reactive group able to react, for instance, with a difunctional reagent instantaneously to produce a crosslinked material. The crosslinking of PVC-OH, obtained by chemical modification of the VC–VAc copolymer during processing, by reaction with HMDI, was studied as a function of the number of OH groups present in the polymer (it is expressed as the time of the alcoholysis reaction), crosslinking time during processing, and crosslinking agent concentration.

Concerning the evolution of the crosslinking during processing, Figure 6 shows three plots with rheograms of polymers crosslinked in different conditions. In each part of this figure, two of the above-mentioned variables was kept constant and the third was varied. Figure 6(a) corresponds to runs 13, 14, and 15 reported in Table II. In all of them, the concentration of the polymer, alcohol, and crosslinking agent are the same. The crosslinker was added at 4, 7.5, and 15 min of processing. It was previously deduced that by increasing the processing time the concentration of OH increases and so does the crosslinking points, that is, 15 > 14 > 13. Therefore, it is expected that the torque value was 15 > 14 > 13, as was obtained qualitatively in Figure 6(a).

Figure 6(b) corresponds to runs 15, 18, and 19 reported in Table II. In all of them, the amount of the polymer and alcohol and processing time are the same, the difference being in the amount of



Figure 4 Evolution with processing time of IR spectrum of VC-*co*-VAc processed in the presence of DOP + 1-octanol + DBTO at 40 rpm and 160°C (run 10): (a) initial; (b) at 20 min; (c) at 40 min.

isocyanate 1, 0.3, and 0.5 g, respectively. It is expected the number of crosslinking points, 15 > 19 > 18, and the torque value follow the same order, as observed in Figure 6(b). The fact that the three rheograms were similar during the 15 min of processing gave evidence of the reproducibility of the process and that the alcoholysis/ crosslinking reaction in the VC–VAC polymer is controlled by the processing parameters of temperature, shear, and time.

Figure 6(c) corresponds to runs 14, 16, and 17 from Table II. In this figure, the crosslinking time is varied at 0.5, 1, and 2 min, respectively. According to the above discussion, the torque value will be 17 > 16 > 14, as was obtained. In all the cases, it is shown that there exists a qualitative



Figure 5 Evolution with processing time of the ratio $I[1740 \text{ cm}^{-1}]/I[1428 \text{ cm}^{-1}]$ for different processing temperatures: (\bigcirc) 140°C; (\blacktriangle) 150°C; (\Box) 160°C; (\bullet) 170°C.



Figure 6 Dependence of rheological behavior on crosslinking variables of run 11. (a) Dependence on processing time [NCO]/[OH] = 1 and $t_{\rm cross.} = 0.5$ min; () 4 min; () 7.5 min; (•) 15 min. (b) Dependence on the ratio [NCO]/[OH]; $t_{\rm process.} = 15$ min and $t_{\rm cross.} = 0.5$ min: () 0.3; () 0.5; (•) 1. (c) Dependence on crosslinking time; $t_{\rm process.} = 7.5$ min and [NCO]/[OH] = 1: () 0.5 min; () 1 min; (•) 2 min.

relationship between the final torque value reached after the addition of the crosslinking agent and the expected degree of crosslinking, although only semiquantitative determinations can be withdrawn from these values. In Figure 7, the results obtained concerning the gel content are reported. Plot 7(a) shows that by increasing the reaction time of the alcoholysis higher gel contents are obtained, as a consequence of the formation of a greater number of



Figure 7 Dependence of gel content on crosslinking variables of run 11. (a) Dependence on processing time; [NCO]/[OH] = 1 and $t_{\rm cross.} = 0.5$ min. (b) Dependence on the ratio [NCO]/[OH]; $t_{\rm process.} = 15$ min and $t_{\rm cross.} = 0.5$ min. (c) Dependence on crosslinking time; [NCO]/[OH] = 1 and $t_{\rm process} = 7.5$ min (black bars) or $t_{\rm process.} = 15$ min (gray bars).



Figure 8 Dependence of the (dots) Young's modulus and (bars) gel content on crosslinking variables of run 11. (a) Dependence on processing time; [NCO]/[OH] = 1 and $t_{\rm cross.} = 0.5$ min. (b) Dependence on the ratio [NCO]/[OH]; $t_{\rm process.} = 15$ min and $t_{\rm cross.} = 0.5$ min. (c) Dependence on crosslinking time; $t_{\rm process.} = 7.5$ min and [NCO]/[OH] = 1.

crosslinkable OH groups, reaching 100% of the gel after 15 min of reaction. Plot 7(b) shows that the effect of the [isocyanate]/[OH] ratio on the gel content is lower than expected (it must be noted here that what is employed is the concentration of the isocyanate groups, not diisocyanate molecules). It is due to the high yield of the crosslinking reaction, in the way that small amounts of the crosslinking agent react quantitatively with some of the OH groups and form an insoluble network. The use of greater amounts of isocyanate affects directly the crosslinking density but only slightly to the gel content.

Finally, in Figure 7(c), the effect of the crosslinking time in processing is shown. In this case, it is necessary to make a difference between the crosslinking of polymers with a high or low content of OH groups. In the latest case (black bars in the figure), increasing of the crosslinking time leads to higher gel contents, because a minimum time is necessary to obtain the reaction of two OH groups in two different polymer chains to give a crosslinking point. On the other hand, for polymers with a great number of OH groups (gray bars in figure), a short time gives a high degree of crosslinking and the processing causes the mechanical degradation of the material, and thus the gel content decreases as crosslinking time increases.

In conclusion, the results show that it is possible to obtain materials crosslinked to different degrees as a function of the number of OH groups present in the polymer (processing time) and the concentration of the crosslinking agent. On the other hand, the time of processing after the addition of the diisocyanate is a critical parameter on which depends the homogeneity of the crosslinking, the extent of this reaction, and the possibility of causing degradation of the material.

Mechanical Properties of Crosslinked Polymers

The evaluation of the mechanical properties of crosslinked polymers was carried out using a study of the strain-stress curves obtained in the tensile test at 140°C. In Figures 8 and 9 are shown the results obtained for the Young's modulus and the ultimate tensile strength (UTS) for the same series of samples used in the study of the gel content, whose results are also included in the figures (bars). In all the plots, crosslinked materials are compared with the noncrosslinked polymer processed for 4 min, with the same conditions of the crosslinked polymer and with a common plasticized PVC, using DOP as a plasticizer.

All the results point out that the mechanical properties in crosslinked materials are improved as the gel content increases. In the first approach, it is shown that the crosslinking of PVC-OH during processing leads to plasticized materials with an increase up to 600% of the Young's modulus and up to 1300% in the UTS. However, the effect of each one of three variables studied—time of processing, crosslinking agent concentration, and



Figure 9 Dependence of the (dots) UTS and (bars) gel content on crosslinking variables of run 11. (a) Dependence on processing time; [NCO]/[OH] = 1 and $t_{\rm cross.} = 0.5$ min. (b) Dependence on the ratio [NCO]/[OH]; $t_{\rm process.} = 15$ min and $t_{\rm cross.} = 0.5$ min. (c) Dependence on crosslinking time; $t_{\rm process.} = 7.5$ min and [NCO]/[OH] = 1.

crosslinking time in processing—on the Young's modulus and UTS is different.

In the case of polymer networks with a low density of crosslinks—as is our case considering the low VAc content in the VC–VAc copolymer used (=5%)—all mechanical properties depend strongly on the gel content; nevertheless, UTS, especially, has a great dependence on slight changes in the crosslinking density. Figures 8 and 9 show the dependence on the crosslinking variables of the Young's modulus and UTS, respectively. From Figure 8 it is deduced that the Young's modulus increases as the gel content increases; thus, this parameter depends on the crosslinking variables in the same way as does the gel content.

Similar behavior is found in Figure 9 for the UTS, but this magnitude reveals a great dependence on the time of processing after the crosslinking agent addition [Fig. 9(c)] at high gel contents, which is due to the higher crosslinking density and the homogeneity in the network as the dispersion of the crosslinking agent is improved. However, it is important to note here that too long times of processing after the crosslinking agent addition could cause mechanical degradation in the material and will lead to worse mechanical properties, as is pointed out above.

CONCLUSIONS

The results of this work show the possibility of obtaining hydroxylated PVC via a transesterification reaction during the processing of VC-*co*-VAc copolymers in the presence of an alcohol. The qualitative results indicate a dependence of the transesterification reaction on the alcohol chemical nature and the processing temperature. In comparison to 1-butanol, the best results were obtained with 1-octanol due to its higher molecular weight. On the other hand, it is possible to increase the transesterification reaction rate by increasing the temperature up to 170° C, using processing times up to 25 min, without degradation or crosslinking of the polymer.

The crosslinking of the PVC-OH obtained with HMDI during the processing is also feasible. It leads to polymer networks with a gel content and mechanical properties depending on the cross-linking variables such as the time of processing for transesterification to occur, crosslinking agent concentration, and time of processing after cross-linking agent addition. The results show that by optimizing these three parameters it is possible to greatly increase the mechanical properties at temperatures above the T_{g} .

We are grateful to the Comision Interministerial de Ciencia y Tecnología (CICYT) for financial support (MAT96-0615).

REFERENCES

- Carraher, C. L. E.; Tsuda, M. Modification of Polymers; ACS Symposium Series; American Chemical Society: Washington, DC, 1980.
- Carraher, C. L. E.; Moore, J. Modification of Polymers; Plenum Press: New York, 1983.

- Lazar, M.; Bleha, T.; Rychlý, J. In Chemical Reactions of Natural and Synthetic Polymers, Kemp, T. J., Ed.; Ellis Horwood: Chichester, 1989.
- 4. Marechal, E. Comprenhensive Polymer Science; Chemical Modification of Synthetic Polymers; Pergamon: Oxford, 1989, Vol. 6, Chapter 1.
- 5. Lambla, M. Macromol Symp 1994, 83, 37.
- Lambla, M. Comprehensive Polymer Science; Reactive Processing of Thermoplastic Polymers; Pergamon: Oxford, 1992; first supplement, Chapter 21.
- 7. Tzoganakis, C. Adv Polym Tech 1989, 9, 321.
- 8. Xantos, M. Reactive Extrusion; Hanser: New York, 1992.
- 9. Ratzsch, M. Makromol Chem Macromol Symp 1987, 2, 165.

- Mijangos, C.; Cassagnau, P.; Michel, A. J Appl Polym Sci 1992, 44, 2019.
- Lambla, M.; Druz, J.; Bouilloux, A. Polym Eng Sci 1987, 27, 1221.
- 12. Mijangos, C.; Hidalgo, M. Polymer 1994, 35, 348.
- Mijangos, C.; López, D. Macromolecules 1995, 28, 1369.
- 14. Reinecke, H.; Mijangos, C. Polym Bull 1996, 36, 13.
- 15. Reinecke, H.; Mijangos, C. Polymer 1997, 38, 2294.
- 16. Reinecke, H.; Hidalgo, M.; Mijangos, C. Macromol Chem Rapid Commun 1996, 17, 15.
- López, D.; Reinecke, H.; Hidalgo, M.; Mijangos, C. Polym Int 1997, 44, 1.