

Crosslinking of Natural and Polybutadiene Rubbers with Thiuram Sulfur Donors in the Presence of a Thiuram Monosulfide

J. L. Valentín, A. Rodríguez, A. Marcos-Fernández, L. González

Instituto de Ciencia y Tecnología de Polimeros del CSIC, C/ Juan de la Cierva, 3, 28006 Madrid, Spain

Received 8 July 2003; accepted 18 February 2004

DOI 10.1002/app.20617

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The influence of tetramethylthiuram monosulfide (TMTM) in the vulcanization process of natural rubber and butadiene rubber with dipentamethylene thiuram tetrasulfide (DPTT) was investigated. Vulcanization parameters as reaction rate and reversion varied when TMTM was added in NR-DPTT formulations. Crosslinking density and proportion of monosulfidic crosslinks increased with TMTM content increase. However, a drop in physical properties was observed at high TMTM content and at long times of curing well over t_{97} . Formation of densely crosslinked areas due to polymerization reaction was postulated as the origin

of these variations. In BR-DPTT compounds, torque and monosulfidic crosslink proportions increased when TMTM was added. Polymerization reaction takes place in BR systems too. However, in BR vulcanizates, C—C bonds decreased with TMTM proportion, whereas in NR vulcanizates increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1756–1761, 2004

Key words: vulcanization; networks; elastomers; crosslinking; mechanical properties

INTRODUCTION

Since the discovery by Goodyear of the vulcanization process, and despite decades of applied and fundamental research, some essential aspects about curing mechanisms by sulfur-accelerant and peroxide are not clear.¹

Analytical techniques such as nuclear magnetic resonance (NMR), mass spectrometry (MS), and infrared (IR) and Raman spectroscopy can be applied, but always with difficulties, and they cannot discriminate between different reactions that take place at the same time.^{2–4}

For several years, our laboratory has released work on the existence of different mechanisms and reactions taking place during vulcanization of diene rubbers by peroxide and sulfonylazide derivatives.^{5–10}

Kruger and McGill studied the different crosslink reactions by using low molecular weight polyolefins as vulcanization models, along with studies on sulfuration processes and structure of the resulting network.¹¹

Within this context, the work presented here claims to examine the crosslinking of natural rubber (NR)

and polybutadiene rubber (BR) with the sulfur-donor dipentamethylene thiuram tetrasulfide (DPTT). This sulfurating agent reacts with rubber chains to form C—S bonds. In this study, no sulfur was added to the formulations, and ZnO and stearic acid were included as activators. The presence of ZnO catalyzes the formation of the sulfurating agents and improves the crosslink efficiency.^{12–15}

This article is a continuation of the work on the vulcanization with sulfur donors¹⁶ done in our laboratory. A thiuram monosulfide (TMTM) was included in the formulations. This accelerant of vulcanization affects the rate and efficiency of crosslink reaction as well as the structure of the crosslinks formed.¹⁷

EXPERIMENTAL

Materials

The natural rubber was based on standardized NR (NR SMR), provided by Malaysian Rubber Board (Kuala Lumpur, Malaysia). The polybutadiene rubber, *Intene* 50, was provided by Enichem Polimeri Europa (Milano, Italy) with the following isomeric distribution: 1,4-*cis*, 35 wt %; 1,4-*trans*, 45 wt %; and 1,2-*vinyl*, 20 wt %.

The crosslinking was effected by using DPTT and TMTM provided by Flexsys (Brussels, Belgium).

The toluene, heptane, piperidine, propane-2-thiol, hexane-1-thiol, and methyl iodide (Fluka) were of laboratory grade.

Correspondence to: L. González (lgonzalez@ictp.csic.es).

Contract grant sponsor: CICYT; contract grant number: MAT 2001-1634.

Blending and curing

The master batches were compounded on a two-roll mill, at a temperature of 40–50°C. Measurements of degree of curing were conducted in a Moving Die Rheometer (Model MDR 2000 E, Alpha Technologies, Wilshire, UK). All samples were cured in a thermostatic fluid heated press.

Physical testing

The physical properties were determined on the specimens cured at their respective optimum times (t_{97} of the rheometer) and other cure times.

The tensile properties were measured according to ISO 37 with an Instron Tensile Tester (Model 4301, Instron Ltd., Buckinghamshire, UK), with a grip separation speed of 50 cm/min. The test samples were cut out from the vulcanized sheets by using a microtensile dumbbell-type die. All tensile results reported are the average value of five tests.

Determination of crosslink density, type, and distribution

Equilibrium swelling in toluene was used to determine the crosslink density of the different compounds. Test samples were placed in reagent grade toluene and allowed to reach equilibrium swelling at 30°C (~3 days). The samples were blotted with tissue paper and immediately weighed on an analytical balance to the nearest 10^{-4} g, then dried in a vacuum oven for 24 h at 60°C to completely remove the solvent, and reweighed. The V_r value (volume fraction of polymer in the swollen sample) was calculated and the crosslink density of the cured compounds was obtained by using the equation reported by Flory and Rehner.¹⁸

The proportion of polysulfidic crosslinks was determined by using a chemical probe of piperidine-propane-2-thiol, which is capable of cleaving trisulfidic and higher polysulfidic bonds. Toluene-extracted samples were placed under nitrogen in a 0.4M solution of piperidine-propane-2-thiol dissolved in heptane for 6 h. A comparison of the original V_r with the value after probe treatment provides the percentage of polysulfidic links. Conditions for the cleavage of di- and polysulfidic links are by treatment of the vulcanizate with hexane-1-thiol, 1M in piperidine, for 48 h at 25°C.¹⁹

Determination of chemical crosslink concentration, before and after treatment with each of these reagents, allows the calculation of the individual contribution of mono- (plus C—C), di-, and polysulfidic crosslinks to the total degree of crosslink.

Also, the vulcanizates were treated with methyl iodide in mild conditions to break the monosulfidic crosslink while keeping di- and polysulfidic crosslinks

TABLE I
Compounds Formulations (phr)

Compounds	no. 3/0	no. 3/1	no. 3/2	no. 3/3	no. 3/4
Natural rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	1	1	1	1	1
DPTT ^a	3	3	3	3	3
TMTM ^b	0	1	2	3	4

^a Dipentamethylene thiuram tetrasulfide.

^b Tetramethylthiuram monosulfide.

intact. In this way, the existing carbon–carbon crosslinks present in the vulcanizate can be determined.

IR spectra

A FTIR spectrophotometer Model Spectrum One™ (Perkin–Elmer Instruments, Norwalk, CT, USA) was used to record the spectra of the samples. Resolution was 4 cm⁻¹ and the spectra were the average of four scans.

RESULTS AND DISCUSSION

Crosslink reaction of NR with DPTT in the presence of TMTM

In Table I, the formulations for the natural rubber compounds with DPTT and ZnO/stearic acid, and different contents of TMTM, are shown. The crosslinking process was measured with an oscillating die rheometer. The rheograms cured at 150°C are shown in Figure 1. The curing reaction is a first-order reaction, with a very short induction time. The maximum torque increases with TMTM concentration, and the compounds display a flat plateau indicating that, at this temperature, the formed crosslinks are thermally stable. The cure data obtained for the compounds at 150°C are given in Table II. The optimum cure time (t_{97}) values increase with the addition of TMTM. The reversion reaction decreases with TMTM proportion, indicating that the relative content of polysulfidic species decrease when TMTM concentration increase.

In Table III, the physical properties of the compounds cured at 150°C at their optimum times, and at 30 and 60 min, are given. The tensile strength of no. 3/0 compound is very elevated, but, in the presence of TMTM, the values drop to as low as 14.2 MPa for no. 3/4 compound. The shore A hardness increases with TMTM content, suggesting an increase in crosslink density.

When the compounds are cured at 30 min, the tensile strength of the compounds undergoes a very important decrease. For compound no. 3/4, tensile strength is now only 2.7 MPa. The hardness also in-

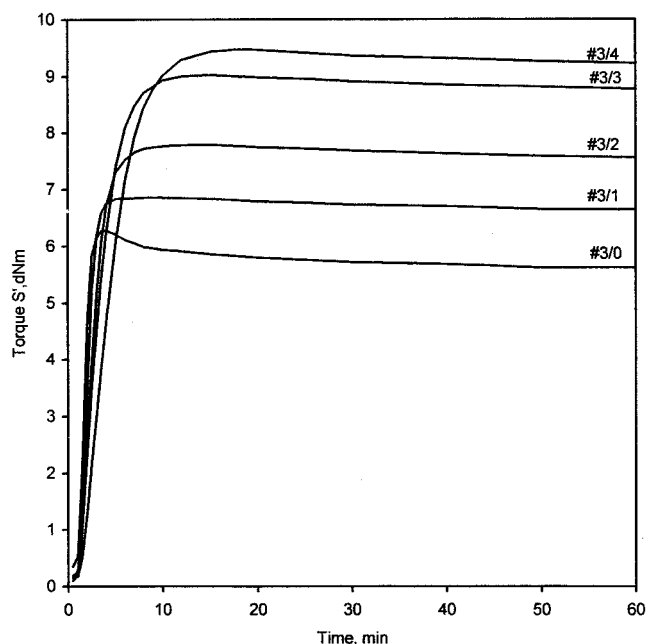


Figure 1 Rheometer curves for compounds 3/0, 3/1, 3/2, 3/3, and 3/4 cured at 150°C.

creases with TMTM content, and therefore, it seems appropriate to assume that an increase in crosslink density was produced. Finally, when the compounds are cured at 60 min, the tensile strength continues its decrease.

Table IV shows the variation in crosslink density for different compounds vulcanized at 150°C for their optimum times and for 30 and 60 min, values measured by equilibrium swelling in toluene and calculated with the Flory–Rehner⁸ method. The table also shows the relative content of the different crosslink types. The compounds with TMTM increase their crosslink density remarkably with the increase of this accelerator. The cure at 30 or 60 min changes the crosslink density only slightly. For compound with DPTT only (no. 3/0), polysulfidic crosslinks are predominant, but the trend is to reduce its proportion when the TMTM content increases, and for compound no. 3/4, the network is composed overwhelmingly of monosulfidic crosslink types.

TABLE II
Rheometer Data for Compounds Cured at 150°C

Compounds	no. 3/0	no. 3/1	no. 3/2	no. 3/3	no. 3/4
t_2 (min)	1.5	1.6	1.7	2.0	2.5
t_{97} (min)	2.9	5.6	6.8	9.6	12.8
T_{max} (dNm)	6.3	6.9	7.8	9.1	9.4
ΔT ($T_{max} - T_{min}$) (dNm)	5.6	6.7	7.5	8.7	9.2
Reversion ^a	11	3.8	2.6	2.4	1.4

$$^a (T_{max} - T_{min}) / (T_{max} - T_{60'}) \times 100.$$

TABLE III
Physical Properties of the Compounds Cured at 150°C for Their Optimum and Other Cure Times

Compounds	no. 3/0	no. 3/1	no. 3/2	no. 3/3	no. 3/4
Cure at t_{97} (min)	2.9	5.6	6.8	9.6	12.8
Hardness, Shore A	39.7	43.7	46.8	48.4	47.8
Elongation at break (%)	750	800	750	600	400
Tensile strength (MPa)	34.0	25.2	25.0	19.0	14.2
Cure time (min)	30	30	30	30	30
Hardness, Shore A	41.2	44.4	47.4	48.2	49.6
Elongation at break (%)	750	750	700	280	260
Tensile strength (MPa)	25.5	21.1	19.5	12.5	2.7
Cure time (min)	60	60	60	60	60
Hardness, Shore A	40.7	44.4	47.2	48.7	49.7
Elongation at break (%)	700	680	660	250	220
Tensile strength (MPa)	20.5	19.2	15.0	3.0	2.5

Crosslink densities for no. 3/4 compound cured at t_{97} , 30 and 60 min are practically identical (see Table IV); however, the tensile strength values are dramatically different, as Table III shows. Networks with a similar number of crosslinks present very different physical properties. These results lead us to think not only that the presence of TMTM in a vulcanization with a sulfur donor such as DPTT produces networks with mainly monosulfidic links, but also another reaction that favors the drop in physical properties must take place.

To account for these results, another reaction and mechanism must be envisaged. One possible explanation is that persulfonyl radicals give rise to the polymerization reaction between adjacent double bonds, decreasing the number of double bonds in the polymer. This fact could be appropriately checked by means of IR spectroscopy. Figure 2 shows the IR spectra of the no. 3/4 compound cured at 150°C for 60 min. The band at 885 cm^{-1} , corresponding to the out-of-

TABLE IV
Change in Crosslink Density for Compounds Cured at 150°C for Their Optimum Cure Time (t_{97}), 30 and 60 min

Compounds	no. 3/0	no. 3/1	no. 3/2	no. 3/3	no. 3/4
Cure at t_{97} (min)	2.9	5.6	6.8	9.6	12.8
Crosslink density (mol/g $\times 10^5$)	8.22	8.68	10.90	12.48	12.58
Total S_x ($x > 2$) (%)	64	33	27	3	8
Total S_2 (%)	28	41	23	36	17
$S_1 + C-C$ (%)	8	26	50	61	75
Cure at 30 min					
Crosslink density (mol/g 10^5)	7.70	9.46	11.1	12.1	12.3
Cure at 60 min					
Crosslink density (mol/g 10^5)	6.35	8.83	10.4	10.70	11.50

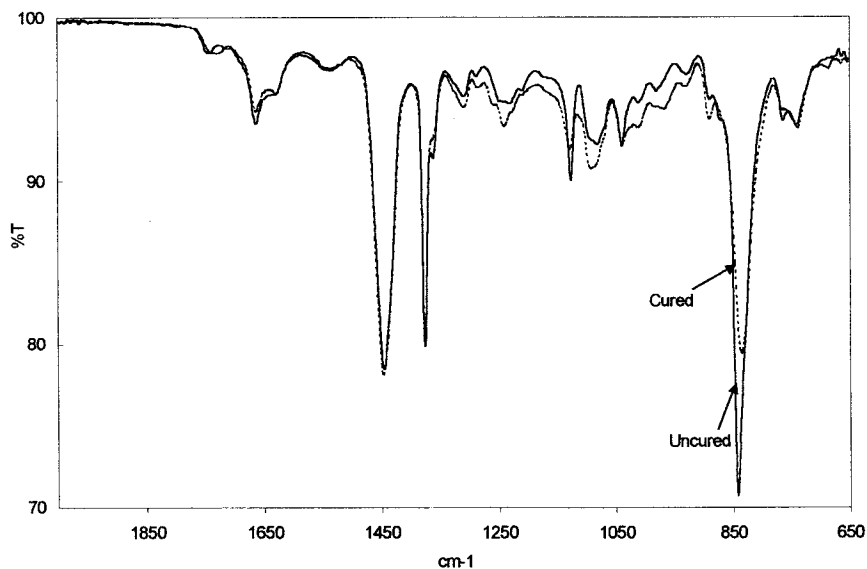


Figure 2 IR spectra of compound 3/4 cured at 150°C for 60 min and uncured rubber.

plane deformation $\gamma(=C-H)$ *cis*, decreases to a considerable extent.

Generally, it is accepted that the failure of an elastomer can be attributed to the presence of an inhomogeneous crosslink distribution. This small but densely crosslinked polymer volume acts at a relatively small deformation as rupture nucleus,²⁰ and these are failure initiation sites. A network with this texture will obviously possess lesser tensile strength than a more uniform network, such as the compound no. 3/0 cured at t_{97} .

Also, the presence of these discrete zones or cluster with high crosslink density should be responsible for the higher hardness values obtained. Nevertheless, with the swelling method used to determine the crosslink density, it is not possible to distinguish a normal crosslink from a cluster.

Crosslink reaction of BR with DPTT in the presence of TMTM

In Table V, the formulations of NR and BR compounds with DPTT and TMTM, with or without ZnO/stearic acid, are shown. The rheograms of the compounds cured at 150°C are shown in Figures 3 and 4.

In a recent articles,⁶ we studied the process of crosslink of NR with DPTT with or without ZnO/stearic acid. The rheogram of compound 3, which contains ZnO/stearic acid, shows a flat, slightly descendent plateau, indicating that, at this temperature, the formed crosslinks are quite stable. On the other hand, compound 4, which contains no ZnO/stearic acid, shows no plateau and an important reduction in torque takes place, probably not due to scission of polysulfidic crosslink, but to another mechanism. The

behavior of BR compounds is surprising. The torque maximum of compound 1 is very high with respect to NR, not presenting reversion at long times. The behavior of compound 2, which contains no ZnO/stearic acid, shows in this case no reversion reaction, contrary to compound 4.

Figure 4 shows the crosslinking progress measured with an oscillating die rheometer at 150°C. The crosslinking reaction rate is similar for compounds 5 and 6. Compound 6, containing DPTT and TMTM, shows a superior torque than that obtained for the compound containing only DPTT. The increase in ΔT , being present for TMTM, can be explained if we consider that the sulfur atoms useful for crosslinking contained on the DPTT molecule do not participate in polysulfidic structures, which means that for the same content of sulphur atoms, more crosslinks are formed.

Formulation 7, with only TMTM, is not able to produce crosslinking. This result confirms that the monosulfenyl radical generated by thermal scission of TMTM is unable to generate crosslinks.

TABLE V
Compounds Formulations (phr)

Compounds	no. 1	no. 2	no. 3	no. 4	no. 5	no. 6	no. 7
Buadiene rubber ^a	100	100	—	—	100	100	100
Natural rubber	—	—	100	100	—	—	—
Zinc oxide	5	—	5	—	5	5	5
Stearic acid	1	—	1	—	1	1	1
DPTT ^b	2	2	2	2	3	3	—
TMTM ^c	—	—	—	—	—	3	3

^a Intene 50.

^b Dipentamethylen thiuram tetrasulfide.

^c Tetramethylthiuram monosulfide.

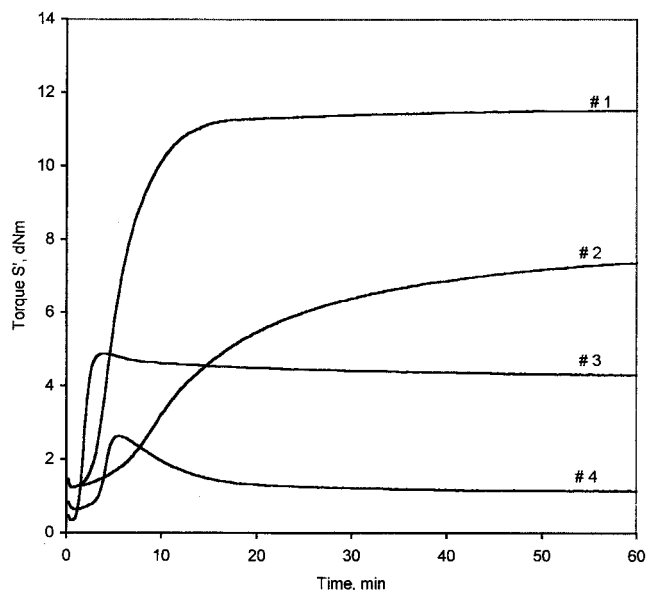


Figure 3 Rheometer curves for compounds 1, 2, 3, and 4 cured at 150°C.

The cure data obtained for the compounds cured at 150°C are given in Table VI. The optimum cure time (t_{97}) value increases with the addition of TMTM. The reversion reaction is null for both compounds, and therefore, the unstable structure ($-S_{x>2}-$) must be almost absent in the rubber network.

Table VII shows the crosslink density for both compounds cured at 150°C for their optimum times, values measured by equilibrium swelling in toluene. Also, the table shows the relative content of the dif-

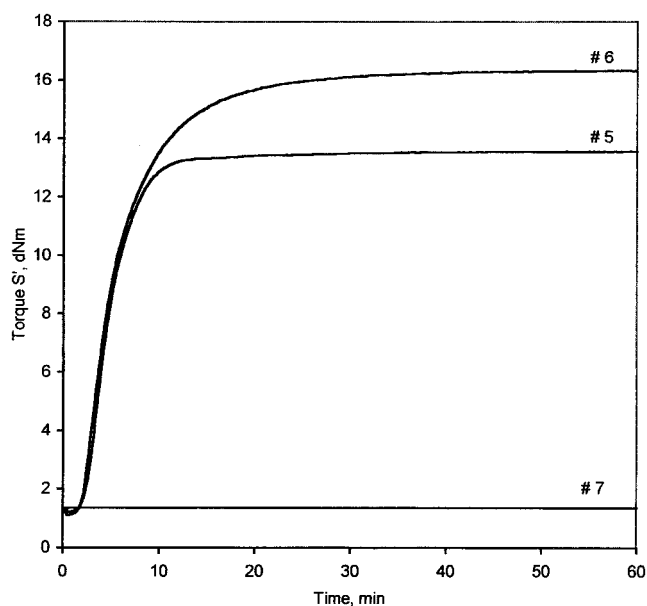


Figure 4 Rheometer curves for compounds 5, 6, and 7 cured at 150°C.

TABLE VI
Rheometer Data for Compounds Cured at 150°C

Compounds	no. 5	no. 6	no. 7 ^a
t_{97} (min)	11.9	25.0	—
T_{\max} (dNm)	13.6	16.3	—
ΔT ($T_{\max} - T_{\min}$) (dNm)	12.4	15.2	—
Reversion ^b	Null	Null	—

^a No curing.

^b $(T_{\max} - T_{\min}) / (T_{\max} - T_{60'}) \times 100$.

ferent crosslink types that can be found. The crosslink density of BR compounds cured with DPTT is much higher than that obtained in NR compounds for similar formulations (see Table IV). The presence of TMTM (no. 6) leads to a superior crosslink density that can be explained if the TMTM produces preferentially monosulfidic structures. The proportion of monosulfidic species in 6 is effectively much superior to that in the compound with only DPTT.

Compounds 5 and 6 were treated with methyl iodide in appropriate conditions to cleave monosulfidic crosslinks, leaving intact superior sulfidic structures. The treatment allows us to confirm the existence of C—C crosslinks. These C—C crosslinks could be formed by a homopolymerization reaction of the double bonds of the polymer chains and could be initiated by persulfonyl radicals. This point could be appropriately tested by means of IR spectroscopy. The bands at 966, 728, and 911 cm^{-1} (Fig. 2) correspond to the out-of-plane deformation $\gamma(=\text{C}-\text{H})$ *trans*, $\gamma(=\text{C}-\text{H})$ *cis*, and $\omega(=\text{CH}_2)$ *vinyl*, and in the cured compound, a certain decrease is observed with respect to the uncured compound, especially in *cis* and *vinyl* bands.

Surprising is that whereas in NR systems the C—C bonds seem to increase or at least stay low when TMTM content increases [in Table IV, % ($S_1 + \text{C}-\text{C}$) goes from 8 to 75], for BR, the number of C—C crosslinks of compound 5 is higher than that compound 6. For unknown reasons, in compound 6, the presence of TMTM favors the formation of monosulfidic structures, as in NR compounds, but at the same time, the polymerization reaction takes place to a minor extent.

TABLE VII
Distribution of Different Crosslink Types for Compounds Cured at 150°C for Their Optimum Cure Time, t_{97}

Compounds	no. 5	no. 6
Crosslink concentration ($\text{mol/g} \times 10^4$)	8.22	9.68
Total S_x ($x > 2$) (%)	64	33
Total S_2 (%)	28	41
S_1 (%)	8	26
Total C—C (%)	53	17

CONCLUSION

Crosslinking of NR with sulfur donor DPTT in the presence of ZnO/stearic acid produces networks with reverting behavior. The inclusion of TMTM in the formulation practically eliminates reversion, slows the reaction, and increases crosslink density measured by swelling, the effect being increased by the increase in TMTM content.

TMTM favors monosulfidic crosslinks, but at long times well over t_{97} , a drop in physical properties, more important with higher TMTM content, takes place, with almost no reduction in crosslink density. Based on IR spectra, polymerization of double bonds of adjacent chains, leading to densely crosslinked areas, is postulated as the origin of the early failure of the samples when stretched.

For BR/DPTT compounds, with or without ZnO/stearic acid, no reversion is observed and torque achieved is much higher than for NR compounds. Torque increase is higher when TMTM is included in the formulate, and more monosulfidic crosslinks are produced. However, substantial properties of crosslinks are found to be C—C bonds in the formulations with TMTM, becoming predominant in the formulation with only DPTT.

IR spectra confirm the decrease of double bonds in the system and therefore the polymerization reaction. Although polymerization seems to take place in both NR and BR systems, more importantly, in BR systems, no clear explanation can be found to the fact that in BR systems C—C bonds seem to decrease with TMTM, whereas in NR systems, it is not the case.

The authors thank the CICYT for partial support of this research (MAT 2001-1634).

References

1. Nieuwenhuizen, P. J.; Reedijk, J.; van Duin, M.; Mc Gill, W. J. *Rubber Chem Technol* 1997, 70, 368.
2. Zaper, A. M.; Koenig, J. L. *Rubber Chem Technol* 1987, 60, 252.
3. Mori, M.; Koenig, J. L. *Rubber Chem Technol* 1997, 68, 551; 1997, 70, 671.
4. Gonski, W.; Hasenhindl, H.; Freund, B.; Wolff, S. *Kautsch Gummi Kunstst* 1990, 43, 118.
5. González, L.; Rodríguez, A.; de Benito, J. L. *Rubber Chem Technol* 1992, 65, 869.
6. González, L.; Rodríguez, A.; Marcos-Fernández, A.; Chamorro, C. *Kautsch. Gummi Kunstst* 1994, 47, 715.
7. González, L.; Rodríguez, A.; Marcos-Fernández, A.; Chamorro, C. *Rubber Chem Technol* 1996, 69, 203.
8. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. *Polym Int*, to appear.
9. González, L.; de Benito, J. L.; Ibarra, L.; Rodríguez, A.; *J Appl Polym Sci* 1994, 54, 1073.
10. González, L.; Rodríguez, A.; de Benito, J. L.; Marcos-Fernández, A. *J Appl Polym Sci* 1997, 63, 1353.
11. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1991, 42, 2643; 1991, 42, 2651; 1992, 44, 581; 1992, 44, 587; 1992, 45, 573; 1992, 45, 563; 1992, 45, 749; 1992, 45, 755; 1992, 45, 1491.
12. Versloot, P.; van Duin, M.; Duynstee, E. F. J.; Haasnoot, J. G.; Put, P.; Reedijk, J. *Rubber Chem Technol* 1992, 65, 343.
13. Nieuwenhuizen, P. J.; Timal, S.; van Duin, M.; Haasnoot, J. G.; Reedijk, J. *Kautsch Gummi Kunstst* 1998, 51, 336.
14. Hahn, J.; Runk, R.; Schollmeyer, M.; Teimer, V.; Walter, E. *Kautsch Gummi Kunstst* 1998, 51, 206.
15. Nieuwenhuizen, P. J.; Timal, S.; van Veen, J. M.; Haasnoot, J. G.; Reedijk, J. *Rubber Chem Technol* 1998, 71, 750.
16. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. *Rubber Chem Technol* 2000, 73, 89.
17. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. *J Appl Polym Sci* 2002, 48, 4919.
18. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 521.
19. Cennen, J. I.; Rusel, R. M. *Rubber Chem Technol* 1970, 43, 121.
20. González, L.; Ibarra, L.; Rodríguez, A.; Chamorro, C. *Polymer* 1992, 33, 3635.