Polymer Bulletin 58, 923–931 (2007)
DOI 10.1007/s00289-007-0734-4

Polymer Bulletin

Thermal properties of polynorbornene (cis- and trans-) and hydrogenated polynorbornene

Miguel A. Esteruelas[a], Fernando González[b], Juana Herrero[b] (✉), Patricia Lucio[b], Montserrat Oliván[a] and Begoña Ruiz-Labrador[b]

[a]Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain
[b]Departamento de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, 39005
Santander, Spain
E-mail: herreroj@unican.es, Fax: 34-942-201591

Received: 7 September 2006 / Revised version: 9 January 2007 / Accepted: 15 January 2007

Summary

The thermal properties of *trans*-polynorbornene, *cis*-polynorbornene and hydrogenated polynorbornene were examined and its reversibility tested. *Trans*-polynorbornene samples, formed in various solvents, exhibit a softening range, from ambient temperature until 375°C. However, syndiotactic *cis*-polynorbornene samples show a narrower melting range (between 150 and 375°C). The fusion enthalpies of *cis*-polynorbornene samples are around 300-400 J/g. The temperature of decomposition is ca. 456°C (minimum peak DSC) for *trans*-polynorbornene and ca. 466°C, 10°C higher, for *cis*-polynorbornene. The solvent used for the polymerization of norbornene has a negligible influence in the melting temperature range or in the decomposition temperature. The treatment with 2,6-di-*tert*-butyl-4-methyl-phenol during the isolation of polynorbornene leads to materials with different thermal properties. *Trans*-polynorbornene isolated without 2,6-di-*tert*-butyl-4-methyl-phenol exhibited an exothermic peak accompanied by an slight increase in weight (1-2%), while samples treated with 2,6-di-*tert*-butyl-4-methyl-phenol do not show these features.

Introduction

The polymerization of cycloolefins via ring-opening metathesis polymerization (ROMP) is a way to synthesize tailor-made unsaturated polymers [1,2,3]. Among the cycloolefins susceptible to be polymerized by ROMP, norbornene is probably the monomer most studied. In fact, polynorbornene was the first polyalkenamer to be commercialized under the trade name of Norsorex [4,5]. The name polynorbornene comprises polymers with different microstructures. Moreover, the great variability in molecular weights and their distributions make polynorbornene a generic name that range over a whole of polymers that, obviously, should have different properties. *Trans*-polynorbornene is described as an amorphous polymer with a glass transition temperature at 37°C [4,6]. Norbornene polymers crystallize only when the cis component is predominant [7]. However, data about their melting temperature ranges are scarce, while data about enthalpies of fusion are not reported, in contrast to hydrogenated polynorbornene, where they are available [6-9].

ROMP of norbornene by using osmium based catalysts [8,10,11] leads to polymers with a higher *cis* content than those obtained with ruthenium complexes. Recently, Rooney et al. [12] have described the ROMP of norbornene to give high *cis*-polynorbornene (fraction of *cis* double bonds 90%) by using $ReCl_5$ in chlorobenzene and $OsCl_3/PhC{\equiv}CH$ in chlorobenzene/ethanol. They have described effects on the *cis*/*trans* double bond ratio by using different solvents.

We have reported the ROMP of norbornene promoted by the complexes $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os) in different polar and apolar solvents [13]. While the ruthenium complex catalyzes ROMP of norbornene to give *trans*-polynorbornene, the osmium complex leads to syndiotactic *cis*-polynorbornene, 95%, as determined by ^1H NMR spectroscopy. Interestingly, these complexes also catalyze the tandem ROMP-hydrogenation of norbornene giving hydrogenated polynorbornene. These results have allowed us to perform the thermal analysis of *cis*-syndiotactic polynorbornene, *trans*-polynorbornene, and that of hydrogenated polynorbornene. Here we report the thermal properties of *cis*-, *trans*-polynorbornene and hydrogenated polynorbornene obtained using $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os) as catalysts. The effect of the addition of 2,6-di-*tert*-butyl-4-methyl-phenol during the isolation the polymer on the thermal properties has also been studied.

Experimental

ROMP of 2-norbornene and tandem catalysis ROMP-hydrogenation

The reactions were carried out as described elsewhere [13].

Polynorbornene isolation without 2,6-di-tert-butyl-4-methyl-phenol

After stirring for 22 h at 40°C, two different isolation methods were used: (a) when alcohols were used as solvent, the solvent was removed and the white polymer formed washed repeatedly with the alcohol, and dried under vacuum; (b) when toluene or chlorobenzene were used as solvents the solution was poured into stirred methanol (20 mL). The precipitated polymer was recovered by centrifugation, washed several times with methanol, and dried under vacuum.

Polynorbornene isolation with 2,6-di-tert-butyl-4-methyl-phenol

After stirring for 22 h at 40°C, 100 mg of 2,6-di-tert-butyl-4-methyl-phenol was added. The mixture was magnetically stirred at the reaction temperature, 40°C, for (i) 15 minutes or (ii) three hours. Then the polymer was isolated as described in the preceding paragraph.

Thermogravimetry and Differential Scanning Calorimetry (TGDSC)

TGDSC was carried out in nitrogen (or helium) flow of 20 $cm^3{\cdot}min^{-1}$at a heating rate of 10 $K{\cdot}min^{-1}$ from 25°C to 800°C. The reversibility experiments have been performed heating the sample to 200°C, cooling it to 25°C, and then heating again from 25 to 800°C. This is what we call second run. For hydrogentated polynorbornene, third and four runs have also been registered. The samples, 10 mg, were placed in a crucible, part of a Setaram TGDSC 111 instrument.

Results and Discussion

Thermal properties of cis-polynorbornene

Figure 1 shows TGA and DSC curves for *cis*-polynorbornene samples prepared in different solvents. They can be divided in three regions for the purpose of the study. The first one, from ambient temperature until approximately 150°C shows a percentage of weight loss, generally lower than 5%, that is associated to removal of the sorbed solvent. In the second region, between 150° and 350°C, there is no loss weight, while in the third region, near 460°C (462°C minimum DTG, 466°C minimum DSC) decomposition of the sample takes place. The differences between the *cis*-polynorbornenes prepared in different solvents using as catalyst the osmium complex, $OsHCl(CO)(P^iPr_3)_2$, are limited to the first part of the curve, and the temperature at which the weight loss occurs is directly related with the boiling point of the solvent used for the synthesis of the polymer.

Table 1. TGDSC data for (75-95%) *cis*-polynorbornene samples formed in various solvents in presence of $OsHCl(CO)(P^iPr_3)_2$

Solvent	Melting range (°C)	ΔHf (Jg^{-1})	Tm (°C)
Toluene	175-385	437	280
chlorobenzene	197-390	368	325
ethanol	225-375	-	327
ethylenglicol	126-390	345	175
1-propanol	160-390	417	282
2-propanol	150-386	316	275
1-butanol	180-397	376	280
tert-butanol	160-350	-	320
acetone	171-398	289	290

DSC curves are divided in three regions analogously as TGA curves. All DSC curves show an endothermic peak associated with solvent loss. At lower temperature, between 30 and 40°C, this endothermic peak shows a shoulder. This feature may be due to the glass transition temperature (T_g) of the polymer, as there is no simultaneous weight loss. In this context, we note that 20% *trans*-polynorbornene has a T_g at 37°C [6]. Between 150 and 350°C there is a somewhat broad heat adsorption without mass loss indicating melting of the sample (Figure 1). All these *cis*-polynorbornene samples exhibit analogous curves. Melting ranges for this broad endothermic heat flow as well as fusion enthalpies associated with it have been measured and are collected in Table 1. The approximate melting peak temperatures are also showed. Melting enthalpies range between 290 and 437 J/g for all samples. As far as we know fusion enthalpies of polynorbornene have not been reported.

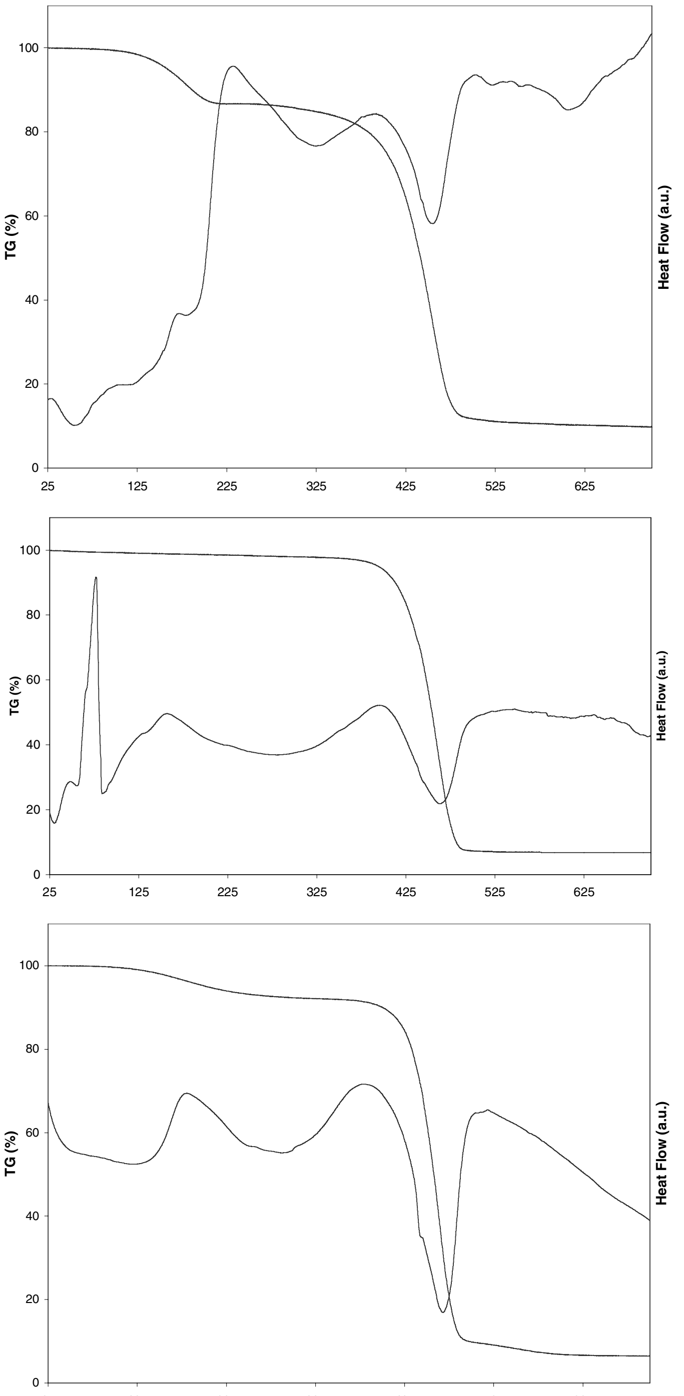

Figure 1. TGA and DSC curves for *cis*-, syndiotactic polynorbornene obtained in presence of the osmium complex, $OsHCl(CO)(P^iPr_3)_2$, and in various solvents: ethanol, 1-propanol and acetone (from top to bottom).

At 466°C (minimum of the heat flow), and associated to ca. 97% weight loss, a strong heat adsorption takes place, indicating the decomposition of the sample. The decomposition temperature for all the *cis*-polynorbornene samples tested is around this temperature. In some samples we observe a small shoulder at 441°C, which is probably due to the small fraction of *trans*-polynorbornene present in the sample.

Thermal properties of trans-polynorbornene

We have reported TGA and DSC curves for *trans*-polynorbornene [13]. In the DSC curve there is a change of the baseline at ca. 30°C, which is probably due to the glass transition temperature. At about 90°C an exothermic peak associated with a slight weight increase 1-2% is observed (Figure 2, top). Brumaghim and Girolami [14] have also observed a similar weight increase. After these features a continuous heat adsorption until 350°C without mass loss is observed, as expected for an amorphous polymer. This is due to a continuous softening of the sample from ambient temperature until near decomposition. Decomposition of the sample takes place at 456°C (minimum of the heat flow, and 452°C minimum DTG), ca. 10°C lower than *cis*-polynorbornene. There are little differences between samples prepared in different solvents, as it occurs for *cis*-polynorbornene.

We have described [13] that both features, exothermic peak and weight increase, (i) are not reversible after the temperature is raised; (ii) the same behavior is observed under helium and (iii) the weight gain depends on the crucible exposed surface. It appears that the expanded structure of polynorbornene can incorporate not only liquid aromatic compounds [4] but also gases.

In order to support this hypothesis, two different methods have been used to isolate the polymer: in the absence, and in the presence of 2,6-di-*tert*-butyl-4-methyl-phenol. 2,6-di-*tert*-butyl-4-methyl-phenol is known to be an inhibitor of radical polymerization, responsible of the cross-linking of the polymer after isolation [15]. Once the polymerization process is finished and before isolation of the formed polymer, the inhibitor was added. If the resultant suspension was stirred for 15 minutes no weight increase was observed but an exothermic peak is showed, although of lesser heat than that of the sample isolated without 2,6-di-*tert*-butyl-4-methyl-phenol (Figure 2, center). After stirring for three hours, no exothermic peak or weight increase is observed in the resulting polymer (Figure 2, bottom). All samples treated with 2,6-di-*tert*-butyl-4-methyl-phenol do not show exothermic peak nor weight gain. Thus, addition of 2,6-di-*tert*-butyl-4-methyl-phenol after polymerization and before isolation modifies polymer properties.

Thermal properties of hydrogenated polynorbornene

We have reported that the complexes $MHCl(CO)(P^iPr_3)_2$ (M = Ru, Os) catalyze the tandem ROMP-hydrogenation of norbornene. The hydrogenation step is carried out at 3 atm of H_2 [13]. For comparative purposes, the hydrogenation of the polymer has also been carried out by the diimide hydrogenation method. Thermal analysis of hydrogenated polynorbornenes obtained using both methods show TGA curves as those shown on Figure 3. There is no weight loss from ambient temperature until 430°C. At this temperature decomposition of the sample begins. DTG minimum at 480°C was used for the determination of the polymer decomposition temperature. The

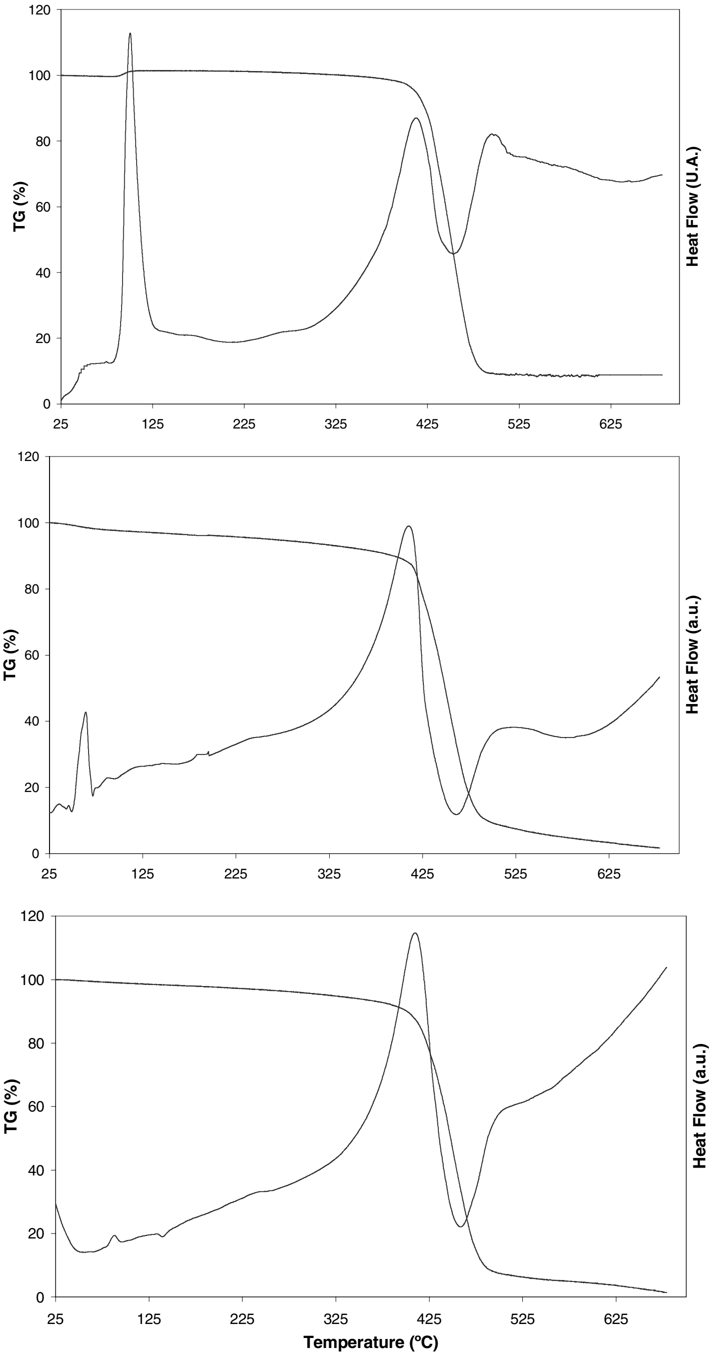

Figure 2. Effect of the addition of 2,6-di-*tert*-butyl-4-methyl-phenol during isolation of the polymer. TGA and DSC curves for *trans*-polynorbornene obtained 2-propanol in presence of the ruthenium complex, $RuHCl(CO)(P^iPr_3)_2$ and isolated: (from top to bottom) without 2,6-di-*tert*-butyl-4-methyl-phenol; after 15 minutes of stirring with 2,6-di-*tert*-butyl-4-methyl-phenol; after three hours of stirring with 2,6-di-*tert*-butyl-4-methyl-phenol.

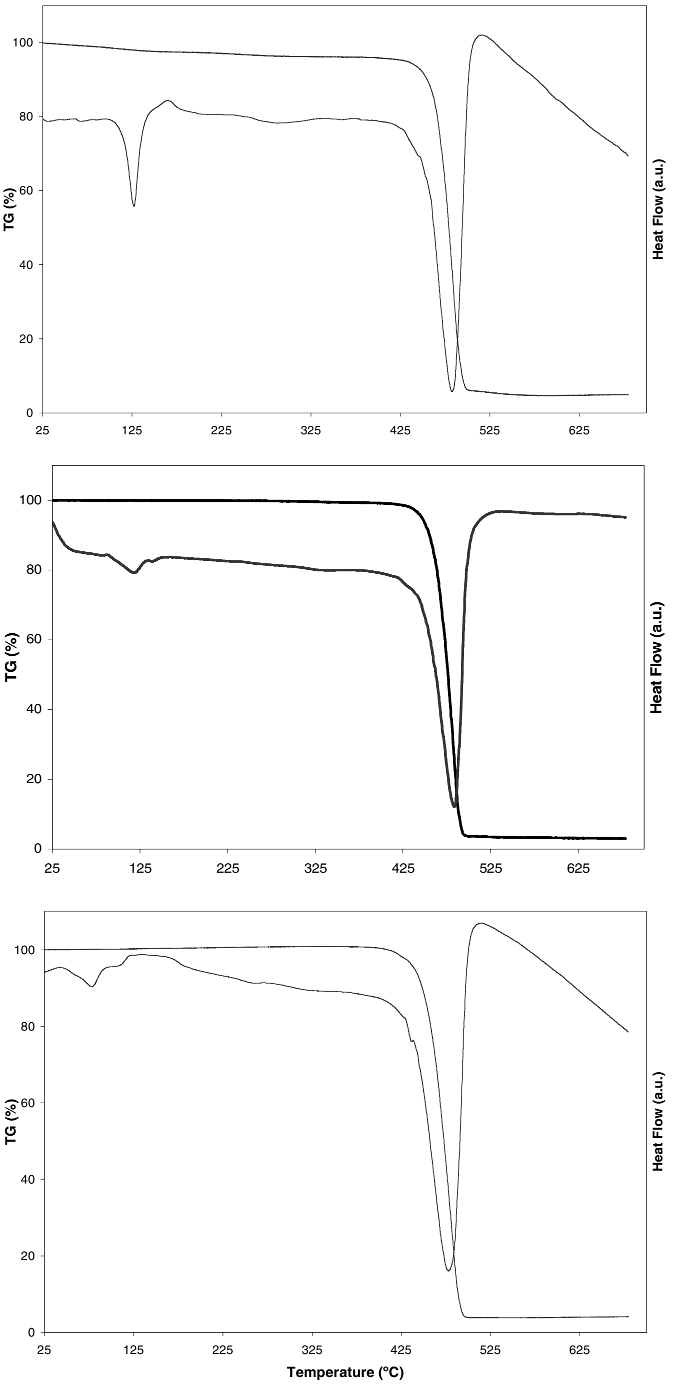

Figure 3. TGA and DSC curves for hydrogenated polynorbornene obtained by ROMP of norbornene with $OsHCl(CO)(P^iPr_3)_2$ and hydrogenated: (from top to bottom) with *p*-toluene sulfonyl hydrazide; with $OsHCl(CO)(P^iPr_3)_2$ as catalyst under three atmospheres hydrogen pressure; with $OsHCl(CO)(P^iPr_3)_2$ as catalyst under one atmosphere hydrogen pressure.

DSC curve of hydrogenated polynorbornene obtained by the diimide hydrogenation method contains two well-defined endothermic peaks (Figure 3, top). The first one at 110°C is due to the melting of the polymer. The measured fusion enthalpy is 22 J/g. The second one, at 483°C (heat flow minimum), is associated to the decomposition of the sample. Other samples of hydrogenated polynorbornene prepared under similar conditions show similar curves with variations on the melting temperature (Tm) and fusion enthalpy. Both, polymer melting temperatures and fusion enthalpies are collected in Table 2.

Table 2. TGDSC data for hydrogenated polynorbornene

Preparation Polymerization/ Hydrogenation	Tm (°C)	ΔH_f (Jg^{-1})
Os/2-propanol/ P_{H2}=1at [a]	116	13.7
Os/2-propanol/ P_{H2}=3at	87/110[b]	24.6
Os/toluene/ P_{H2}=3at, 2days [a]	110	22.0
Os/toluene/ P_{H2}=3at, 9days	152	50.3
Os/2-propanol/ p-tolsfhyd	127	37.5
Ru/2-propanol/ P_{H2}=3at	138	22.0
Ru/toluene/ P_{H2}=3at	133	38.0
Ru/2-propanol/ p-tolsfhyd	139	39.6
$OsCl_3$/PhC≡CH/p-tolsfhyd	115	26.3
Ref [6, 9]	140.8	58.7

p-tolsfhydr=*p*-toluene sulfonyl hydrazide. [a] Second run. [b] Two peaks.

The reversibility of both melting temperature and fusion enthalpy of the hydrogenated polynorbornene obtained by polymerization with the system formed by $OsCl_3$/PhC≡CH and subsequent hydrogenation with *p*-toluene sulfonyl hydrazide has also been tested. In the second run, the melting temperature decreased slightly from 115°C to 111°C, while the fusion enthalpy was almost constant, 26 J/g. Third and four runs lead to similar values. Hydrogenation of polynorbornene by the *p*-toluene sulfonyl hydrazide method gives a hydrogenated sample that shows melting temperature and enthalpy of 140.8°C and 58.7 J/g [9]. The first polynorbornene fully hydrogenated by catalysis leads to a sample with a melting temperature of 136°C [16]. We have also observed that the crystallinity of the hydrogenated polynorbornene obtained by hydrogenation with molecular hydrogen decreases if the hydrogenation step is carried out in 1 atm of H_2 (Figure 3, center and bottom). This can be related with a higher degree of unsaturation in the polymer [17].

Conclusions

Cis-polynorbornene can be distinguished from *trans*-polynorbornene by thermal analysis. Samples of *cis*-polynorbornene that differ on the solvent in which they have been prepared show a narrower melting range than *trans*-polynorbornene, which is amorphous. The addition of a radical inhibitor, 2,6-di-*tert*-butyl-4-methyl-phenol, after polymerization and before isolation has a significative influence on the thermal properties of *trans*-polynorbornene. Without 2,6-di-*tert*-butyl-4-methyl-phenol, *trans*-polynorbornene samples exhibit an exothermic peak near 90°C and a simultaneous 2% weight increase. Both features disappear by treatment with 2,6-di-*tert*-butyl-4-methyl-phenol.

Acknowledgements. We acknowledge financial support from the Spanish "Ministerio de Educación y Ciencia" (Project BQU2002-00606). We thank Sonia Conde and Angélica López-Sustacha for technical assistance.

References

1. Ivin KJ, Mol JC (1997) Olefin Metathesis and Metathesis Polymerization. Academic Press, San Diego
2. Grubbs RH, Tumas W (1989) Science 243:907
3. Schrock RR (1993) Ring-Opening Metathesis Polymerization. In: Brunelle DJ (ed) Ring-opening polymerization: mechanism, catalysis, structure, utility. Munich, New York, pp 130-156
4. Ohm RF (1980) Chemtech 10:183
5. Marbach A (1989) Rubber world June:30
6. Galiatsatos V (1999) Poly(norbornene). In: Polymer Data Handbook. Oxford University Press, pp. 698-700
7. Dräxler A (1988) Polyalkenylenes. In: Bhowmick AK, Stephens HL (ed) Handbook of Elastomers: Marcel Dekker, Inc pp. 661-693
8. Michelotti FW, Keaveney WP (1965) J Polymer Science: Part A 3:895
9. Cataldo F (1994) Polymer International 34:49
10. Al-Samak B, Ebrahimi VA, Carvill AG, Hamilton JG, Rooney JJ (1996) Polymer International 41:85
11. Feast WJ, Harrison DB (1991) Polymer 32:558
12. Al Samak B, Amir-Ebrahimi V, Corry DG, Hamilton JG, Rigby S, Rooney JJ, Thompson JM (2000) J Mol Catal A: Chem 160:13
13. Cobo N, Esteruelas MA, González F, Herrero J, López AM, Lucio P, Oliván M (2004) J Catal 223:319
14. Brumaghim JL, Girolami GS (1999) Organometallics 18:1923
15. Denisov ET, Khudyakov IV (1987) Chem Rev 87:1313
16. Abboud W, Revillon A, Guyot A (1989) New Polymeric Mater 1:155
17. Lee L-BW, Register RA (2005) Macromolecules 38:1216