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1,2 Syndiotactic polybutadiene of controlled crystallinity by butadiene-isoprene copolymerization with $CrCl_2 \cdot (dmpe)_2$-MAO

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Summary

$CrCl_2 \cdot (dmpe)_2$-MAO gives crystalline 1,2 syndiotactic polymers from butadiene and 3,4 atactic polymers from isoprene. Butadiene-isoprene copolymerization gives copolymers in which butadiene and isoprene units have respectively a 1,2 and a 3,4 structure. Copolymers with less than 20% isoprene are crystalline, their melting point decreasing from ca. 160°C to ca. 50°C with increasing isoprene content. This makes possible to obtain 1,2 syndiotactic polybutadiene with controlled melting point. Copolymers with more than 20% isoprene are amorphous, with a glass transition temperature in the range 2÷5°C. Copolymer microstructure was determined by ^{13}C NMR.

Introduction

Several types of catalysts have been proposed for the polymerization of butadiene to 1,2 syndiotactic polymer [1-8]. A highly stereoregular polymer with a melting point of about 216°C has been obtained with the system $Co(C_4H_6)(\eta^5\text{-}C_8H_{13})$ / CS_2 [5-8]. In a previous paper we have reported that $CrCl_2 \cdot (dmpe)_2$-MAO also is a highly stereospecific catalyst for the polymerization of butadiene to 1,2 syndiotactic polymer. It is also active for the polymerization of isoprene, giving an atactic polymer with an essentially 3,4 structure [9]. We have now examined the copolymerization of butadiene and isoprene with the chromium catalyst.

In case of random copolymerization, the incorporation of isoprene units into the polybutadiene chain would make it possible to obtain syndiotactic polybutadiene with a melting point regularly decreasing with the isoprene content. Syndiotactic polybutadiene having a melting point < 100°C is of practical interest for use as elastomer, in mixture with other products. It is usually obtained with catalysts consisting of a cobalt compound, an aluminum-alkyl and a modifier; depending on the nature of the latter a 1,2 polybutadiene of different melting point can be obtained [10-15]. E.g., the system cobalt octanoate-MAO-$P(Ph)_3$ gives a 1,2 polybutadiene (~92%) with a melting point ca. 75°C, but if $P(^nBu)_3$ or $P(benzyl)_3$ are used instead of $P(Ph)_3$, an amorphous 1,2 polybutadiene (~85%) is obtained. The melting point of the copolymer cannot be controlled with precision with these catalysts as can be done with the butadiene/isoprene copolymerization.

We were interested in the butadiene/isoprene copolymerization with chromium catalysts also for another reason. Butadiene/isoprene copolymerization has been so far examined only with catalysts that give copolymers with a predominantly 1,4 structure. The reactivity ratios have been reported to be rather similar, independently of the catalyst used [16,17].

The factors that affect reactivity ratios in transition metal catalyzed diene copolymerization are not clear, but they are likely related to the coordination geometry around the transition metal. Therefore, we expected the reactivity ratios for a 1,2 copolymerization to be significantly different from those of a 1,4 copolymerization.

In this note we report on the most significant results of this work.

Experimental part

Materials

$CrCl_2 \cdot (dmpe)_2$ was prepared as described in the literature [18]. Methylaluminoxane (MAO) (Witco, 30 wt.-% solution in toluene) was used without further purification. Toluene (Baker, >99% pure) was refluxed over Na for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen. Butadiene (Air Liquide, >99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to −20°C. Isoprene (Aldrich, 99% pure) was refluxed over CaH_2 for ca. 2 h, then distilled trap-to-trap and stored under dry dinitrogen.

Copolymerization

Butadiene (2 mL) was condensed into a 50 mL dried glass reactor kept at −20°C, then isoprene and toluene were introduced in the order. The solution was brought at the desired temperature; MAO and $CrCl_2 \cdot (dmpe)_2$, as toluene solutions, were then added. The polymerization was terminated with methanol containing little amount of hydrochloric acid, the polymer was coagulated and repeatedly washed with methanol, then dried i. vac. at room temperature.

Polymer characterization

Intrinsic viscosities were determined in toluene at 25°C using a Desreux-Bishof. ^{13}C NMR examination was performed with a Bruker AM 270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 103°C (hexamethyldisiloxane as internal standard). The concentration of the polymer solution was about 10 wt.-%.

The composition of the butadiene-isoprene copolymers was evaluated from ^{13}C NMR spectra by the relationship:

$$B\% = A_B/(A_B+A_I)$$

where $\mathbf{A_B}$ is the total sum of the integrated areas of the resonances around 112 ppm, due to the olefinic CH_2 carbon of the butadiene unit; $\mathbf{A_I}$ is the total sum of the integrated areas of the resonances around 110 ppm, due to the olefinic CH_2 carbon of the isoprene unit. The syndiotactic index ([rrrr]%) was evaluated from the integrated areas of the peaks around 112 ppm , corresponding to the different butadiene pentads, as reported in the literature [19-21].

Differential scanning calorimetry (DSC) scans were performed on a Perkin Elmer Pyris 1 instrument. The sample, ca. 10 mg, was heated from –150°C to 200°C under an helium atmosphere (30 ml/min) with a scanning rate of 20°C/min.

Results and Discussion

The catalyst system $CrCl_2(dmpe)_2$-MAO [dmpe = 1,2-bis(dimethylphosphino)ethane; MAO = methylaluminoxane] polymerizes butadiene to crystalline 1,2 syndiotactic polymers (Table 1, run 1).

Table 1 Butadiene-isoprene copolymerization with $CrCl_2{\cdot}dmpe_2/MAO$ [a)]

Run	*Iso-prene*	*Feed* [b]	*Time*	*Yield*		*Copolymer Composition* [c]		*[η]* [d]	*m.p* [e]	*T_g* [e]	*[rrrr]* [c]
	mL	*I*	*min*	*mg*	*%*	*B*	*I*	*$dL{\cdot}g^{1}$*	*°C*	*°C*	*%*
1	-	0	10	214	15.3	100	0	2.6	162		74.9
2	0.5	16	15	189	10.8	98.5	1.5		152		66.2
3	1	28	15	175	8.3	97.4	2.6		148		67.2
4	2	43.5	17	144	4.2	96.8	3.2		132		61.4
5	3	53.5	20	178	5.2	95.4	4.6		128		62
6	4	61	22	160	3.8	93.5	6.5		123		57.5
7	5	66	24	125	2.6	91.8	8.2		119		55
8	6	70	153	208	3.8	90	10	2.2	107		55.7
9	7	73	160	205	3.0	88.9	11.1	2.2	100		54.1
10	8	75.5	158	187	3.0	85.3	14.7		89		50.6
11	10	79.5	120	474	5.8	83.5	16.5	2.3	49		46.2
12	15	85	155	465	4.0	81	19	2.1	52	5	42
13	20	88.5	212	362	2.4	74	26	1.9		4	37
14	25	90.5	243	360	2	68.5	31.5	2		3	33.4
15	20	94	660	400	2.8	61.6	38.4	1.8		2	25.5
16	2	100	6840	946	69.6	0	100			29	

[a)] Polymerization conditions: toluene (total volume, 30 mL); butadiene, 2 mL (1 mL in run 15; no butadiene in run 16); Cr, $3{\times}10^{-5}$ mol; Al/Cr = 100; +20°C. [b)] Feed composition in mol-%; I = isoprene. [c)] Determined by NMR analysis, as reported in the experimental part; butadiene units have a 1,2 structure while isoprene units a 3,4 structure. [d)] Intrinsic viscosity, determined in toluene at +25°C (run 1, in o-dichlorobenzene at 135°C). [e)] Determined by DSC measurements.

Isoprene too is polymerized by the Cr(II) system, giving an amorphous polymer with an essentially 3,4 structure (a small amount of 1,4 units are also present, less than 5÷6%) in which *mr* triads are predominant (Fig. 1). However, polymerization of isoprene is much slower than that of butadiene (Table 1, runs 1 and 16).

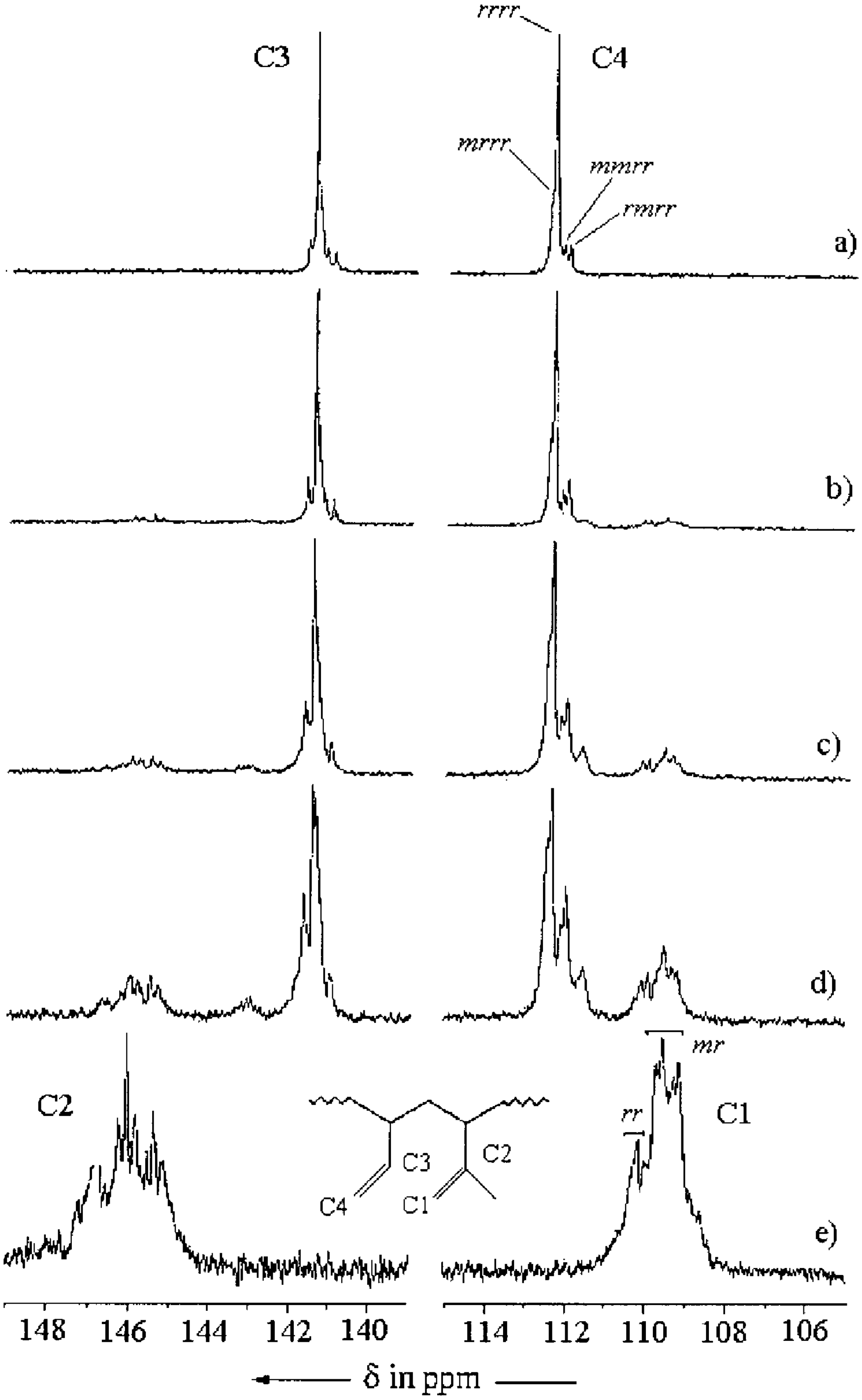

Figure 1. ^{13}C NMR spectra (olefinic region, methylene carbons) of *a)* 1,2 syndiotactic polybutadiene (Tab. 1, run 1); *b)* butadiene-isoprene (90:10 molar ratio) copolymer (Tab. 1, run 8); *c)* butadiene-isoprene (81:19) copolymer (Tab. 1, run 12); *d)* butadiene-isoprene (68.5:31.5) copolymer (Tab. 1, run 14); *e)* 3,4 polyisoprene (Tab. 1, run 16) obtained with $CrCl_2(dmpe)_2$-MAO. Butadiene and isoprene units in the copolymers have 1,2 and 3,4 structure, respectively.

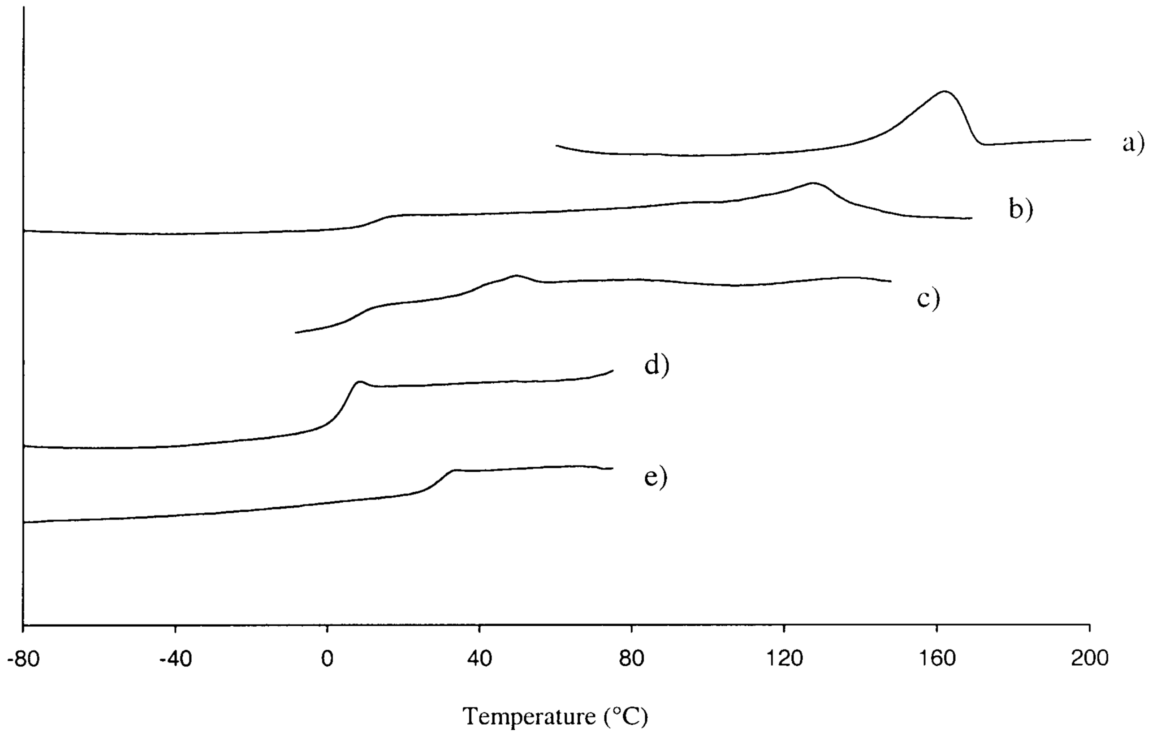

Figure 2 DSC curves of *a*) 1,2 syndiotactic polybutadiene (Tab. 1, run 1); *b*) butadiene-isoprene (93.5:6.5 molar ratio) copolymer (Tab. 1, run 6); *c*) butadiene-isoprene (83.5:16.5) copolymer (Tab. 1, run 11); *d*) butadiene-isoprene (74:26) copolymer (Tab. 1, run 13); *e*) 3,4 polyisoprene (Tab. 1, run 16) obtained with $CrCl_2.(dmpe)_2$-MAO. Butadiene and isoprene units in the copolymers have 1,2 and 3,4 structure, respectively.

In order to obtain a 1,2 polybutadiene with a controlled melting point we have now copolymerized butadiene and isoprene. The results (Table 1) can be summarized as follows:

a) Copolymers with a butadiene content higher than 80% (Table 1, runs 2-12) show the crystallinity of 1,2 syndiotactic polybutadiene by X-ray, the melting temperature decreasing with increasing the amount of isoprene (Fig. 2).

b) Copolymers with more than 20% isoprene are completely amorphous (Tab.1, runs 13-15), with a glass transition temperature in the range 2÷5°C (Fig. 2).

c) As regards the stereoregularity of butadiene sequences in the copolymers, the ^{13}C NMR spectra (Fig.1) show that the peaks corresponding to *mrrr* (112.40 ppm), *mmrr* (112.10 ppm) and *rmrr* (111.96 ppm) pentads are significantly more intense in the copolymers than in the homopolymer. Insertion of isoprene units causes some steric disorder in butadiene syndiotactic sequences. As regards isoprene units, a comparison of the ^{13}C NMR spectra of the homo- and copolymers seems to indicate an increase of *rr* triads with respect to *mr* triads in the copolymers (Fig. 1).

d) By plotting feed and copolymer composition according to the Fineman-Ross equation [22], the following reactivity ratios have been evaluated for the butadiene-isoprene copolymerization:

$$r_1 = k_{11}/k_{12} = 21.9 \qquad r_2 = k_{22}/k_{21} = 0.09$$

$$r_1 \times r_2 = 2 \qquad (M1 = B; M2 = I)$$

Butadiene and isoprene have been copolymerized with $Al(^iBu)_3$-$TiCl_4$, $Al(^iBu)_2Cl$-$CoCl_2$(ethanol complex) and $CpTiCl_3$-MAO. The following reactivity ratios have been reported (M1 = B; M2 = I) [16,17]:

$Al(^iBu)_3$-$TiCl_4$	$r_1 = r_2 = 1$
$CpTiCl_3$-MAO	$r_1 = 4.7$; $r_2 = 0.31$
$Al(^iBu)_2Cl$-$CoCl_2$	$r_1 = 2.3$; $r_2 = 1.15$

These values are significantly different from those evaluated for the copolymerization with the chromium catalyst. They indicate, e.g., that insertion rate of butadiene on a butadiene-ended growing chain is practiclly the same ($TiCl_4$ system) or 2-5 times higher ($CpTiCl_3$ and Co system) than that of isoprene. In the case of the chromium catalyst it is higher by a factor of ca. 20. It is difficult to give at present an interpretation of these results. More data are needed to see if the same phenomenon is observed with other catalysts that give butadiene/isoprene copolymers with a 1,2/3,4 structure.

Conclusions

The copolymerization of butadiene with isoprene using the Cr(II) catalyst of this work yields 1,2/3,4 copolymers, in which the melting point decreases with increasing the isoprene content.

Various catalysts have been proposed, in the patent literature, for the preparation of 1,2 syndiotactic polybutadiene having a controlled degree of stereoregularity. The copolymerization of butadiene with a small amount of isoprene provides a convenient route to this type of products.

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References

1. Natta G, Porri L, Zanini G, Palvarini A (1959) Chim. Ind. (Milan) 41, 1163
2. Natta G (1960) Chim. Ind. (Milan) 42, 1207
3. Bawn C H, North A M, Walker J S (1964) Polymer 5, 419
4. Iwamoto M, Yuguchi P (1967) Polymer Letters 5, 1007
5. Ashitaka H, Ishikawa H, Ueno H, Nagasaka A (1983) J. Polym. Sci., Polym. Chem. Ed. 21, 1853
6. Ashitaka H, Jinda K, Ueno H (1983) J. Polym. Sci., Polym. Chem. Ed. 21, 1951
7. Ashitaka H, Jinda K, Ueno H (1983) J. Polym. Sci., Polym. Chem. Ed. 21, 1989
8. Ricci G, Italia S, Porri L (1988) Polymer Commun. 29, 305
9. Ricci G, Battistella M, Porri L Macromolecules (2001) 34, 5766
10. Dawans F, Teyssie P (1967) Bull. Soc. Chim. Fr. 8, 2930
11. Iwamoto M, Yuguchi S (1967) Polymer Letters 5, 1007
12. Ichikawa M, Takeuchi Y, Tokunaga H, Kinioki A (Japan Synthetic Resin Co., Ltd.) Jpn. Pat. 71 30, 699 (Chem. Abstr. 1973, 79, 60725u)
13. Ueno H, Chizumi K, Ishikawa H, Tsujimoto N, Nakajima K, Aikawa H, Kimura O (Ube

Industries, Ltd.) Japan Kokai 77, 148, 584 (Chem. Abstr. 1978, 88, 171032h)

14. Mori K, Taketomi T, Imaizumi F Nippon Kagaku Kaishi 11, 1982 (1975) (Chem. Abstr.
1976, 84, 74676f)
15. Halasa A F (Firestone Tire and Rubber Co.) U.S. Pat. 3, 914, 210 (Chem. Abstr. 1976, 84, 12574v)
16. Zambelli A, Proto A, Longo P, Oliva P (1994) Macromol. Chem. Phys. 195, 2623
17. Bresler L.S, Dolgoplosk B. A, KolechKova M. F, Kropacheva Ye. N (1963) Vysokomol.
Soyed. 5, 357
18. Girolami G S, Wilkinson G, Gala A M R, Thornton-Pett M, Hursthouse M B (1985) J. Chem. Soc. Dalton. Trans. 1339
19. Mochel V D (1972) J. Polym. Sci. A-1 10, 1009
20. Elgert K F, Quack G, Stutzel B (1974) Makromol. Chem. 175, 1955
21. Ashitaka H, Inaishi K, Ueno H (1983) J. Polym. Sci., Polym. Chem. Ed. 21, 1973
22. Fineman M, Ross S D (1950) J. Polym. Sci. 5, 2352