Polymer Bulletin 9, 132–138 (1983)

Polymer Bulletin

Cationic Copolymerization of Isobutene with 1,1,4,4-Tetramethyl-1,3-Butadiene

Synthesis and Structural Characterization of the Copolymer

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SUMMARY

The copolymerization of isobutene (I) and 1,1,4,4-tetramethyl-1,-3-butadiene (TMB) was carried out easily and for the first time at -30°C, in a homogeneuos medium and using $EtAlCl_2$ as catalyst. The structure of TMB in the copolymer is exclusively trans-1,4 while the monomer distribution, studied by ^{13}C-NMR, is random.

Using the values of the dyad and triad (centered on I) fractions, the reactivity ratios of both the monomers were obtained according to a procedure previously described: $r_I = 2.0 \pm 0.4$ and $r_{TMB} = 0.4 \pm 0.2$.

INTRODUCTION

Recently we have reported on the cationic copolymerization of isobutene (I) with the three geometric isomers of 2,4-hexadiene (HD) (A.PRIOLA et al.) and shown by ^{13}C-NMR analysis that true copolymers are formed.

Furthermore, the distribution of the monomeric units is almost random because there is only a slight tendency toward a block-type structure. These results prompted us to investigate the copolymerization behaviour of the couple I-1,1,4,4-tetramethyl-1,3-butadiene (TMB), in which the diene carries 4 methyl groups in the 1 and 4 positions. This structural feature of TMB permits to elucidate more clearly than in the case of HD the influence of the steric hindrance on the reactivity of the diene and its distribution in the monomer sequences of the copolymer.

The cationic homopolymerization of TMB was previously investigated (MOODY) by using BF_3 as catalyst and a trans-1,4-structure was attributed to the resulting high MW crystalline polymer, on the basis of X-ray analysis data.

Subsequently, KENNEDY and SQUIRES determined the poisoning and transfer coefficients of TMB with respect to the cationic polymerization of I. They discussed also the reactivity of the t-allyl cation, formed as active species during the polymerization of TMB, in the growing-chain process.

0170-0839/83/0009/0132/$01.40

Our results, reported in this paper, show clearly that the steric hindrance existing on the extreme carbons of the diene system of TMB does not prevent the formation of true random I-TMB copolymers, which are here described for the first time.
Furthermore, we have determined the reactivity ratios of both the monomers, by using the monomer sequence fractions obtained from ^{13}C-NMR spectra, as described previously (PRIOLA et al.). In this manner information on the reactivity of intermediate t-allyl carbenium ions during the copolymerization with (I) have been collected. Only data on the reactivity of cyclic t-allyl carbenium ions were reported and previously discussed by ASO and OHARA.

EXPERIMENTAL

TMB was a commercial product of ANIC, obtained by dehydration of 2,3-dimethyl-hexane-2,3-diol. After distillation (b.p. 135°C at 760 mm Hg; VPC purity > 99%) it was stored and handled under dry nitrogen.
Isobutene, solvents and catalysts were purified and used as described previously (CORNO et al.).
Also copolymerization conditions were reported elsewhere (CORNO et al.). However, the copolymerization temperature was -30°C, because below this value TMB shows a tendency to crystallize from the system. Further details are reported in Table I. The copolymer solutions were coagulated twice with an excess of methanol and dried in vacuo overnight at room temperature.
The GPC analysis of a typical sample of I-TMB copolymer showed a symmetric, monomodal MWD curve and this result suggested a homogeneous character of the copolymer.

Table I: CATIONIC COPOLYMERIZATION OF I WITH TMB

Run	$[EtAlCl_2]$ mmol/l	Feed mole fract of I	Conversion (%)	Composition[a] mole fract. of I	$[\eta]$[b] (dl/g)	Tg[c] (°C)
1	1.6	0.66	15	0.78	0.38	-34
2	4.0	0.50	16	0.69	0.36	-30
3	8.1	0.33	20	0.50	0.32	-13
4	8.1	-[d]	18	-	-	+268[e]

Experimental conditions: solvent = n-pentane + CH_2Cl_2(1/1, v/v); I + TMB = 2.0 mol/l; T = -30°C; time = 20 min.

a) Determined by ^{1}H-NMR
b) Determined in cyclohexane at 25°C
c) By DTA analysis
d) TMB homopolymerization experiment
e) Melting temperature

DTA data showed a single Tg whose value changed by changing the copolymer composition (Table I).

The analytical methods adopted were described in previous papers (PRIOLA et al.; CORNO et al.).

RESULTS AND DISCUSSION

Copolymerization of I with TMB

The results of typical I-TMB copolymerization experiments, carried out at -30°C with different feed composition in a homogeneous system and using $EtAlCl_2$ as catalyst, are shown in Table I.

In the same table also the values of the intrinsic viscosity and Tg of the samples are collected. The relatively high values of $[\eta]$, which concern with samples obtained at -30°C, agree with the low value of the chain transfer coefficient of TMB found by KENNEDY and SQUIRES.

The increase of the TMB content increases the Tg value of the copolymer and this result suggests a random distribution of the monomeric units as it will be confirmed (s. below) by the structural characterization.

The data of Table I, associated to those of Table II and concerning some monomer sequence fractions, have been used for calculating the reactivity ratio of both the monomers, according to a procedure already described (PRIOLA et al.). The values are: $r_I = 2.0 \pm 0.4$ and $r_{TMB} = 0.4 \pm 0.2$, where the confidence interval is 68%, i.e. the standard deviation in the approximation of the normal distribution.

Structural Characterization of I-TMB

The aim of the structural characterization of I-TMB has been the identification of the structural units of the diene and the evaluation of the distribution of the monomeric units. IR and NMR spectroscopy were employed.

Fig. 1 shows the ^{1}H-NMR spectrum of a copolymer containing 50.6 mol% of TMB. Downfield, between 5.3 and 5.4 ppm, there is a signal attributable to the proton of the -C= group belonging to the 1,4-structure of the diene. The doublet character of the signal is due to the different position of the signal of these hydrogen atoms belonging to the dyad TMB-TMB relative to the same atoms of the dyads I-TMB and TMB-I.

However, the problem of the monomer distribution will be discussed below.

In the upfield region there is a signal at about 1.4 ppm due to the methylene of I and a signal, with fine structure, between 1.1 and 0.8 ppm attributable to the methyls of the gem-dimethyl groups of I and TMB. The lack of signals in the region around 1.6 ppm points out clearly that there are not methyls in α position with respect to a double bond. Therefore, there is not a detectable amount of 1,2-unit of TMB in the copolymer.

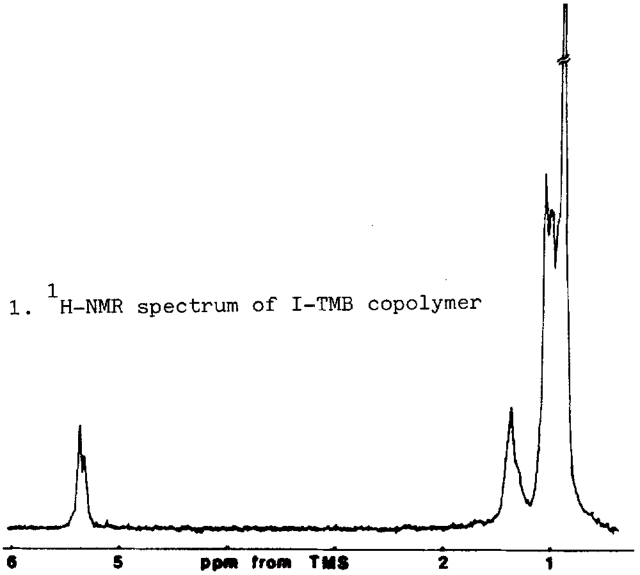

Fig. 1. ^{1}H-NMR spectrum of I-TMB copolymer

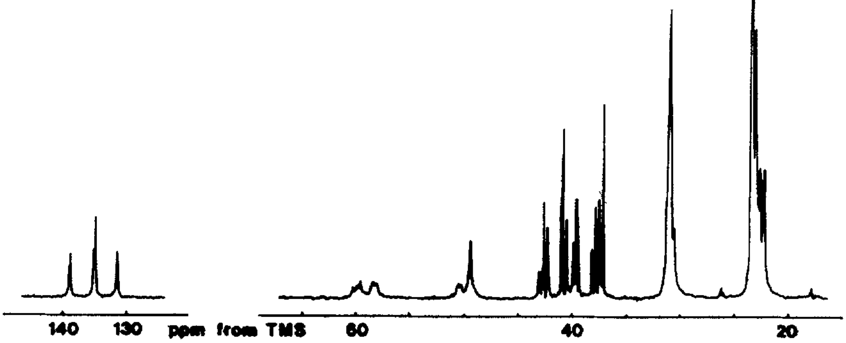

Fig. 2. ^{13}C-NMR spectrum of I-TMB copolymer

The configuration of the double bond of the 1,4-diene unit is clearly trans, according to IR data. In fact, a strong absorption band is present at 985 cm^{-1}, whereas the band typical of the cis-1,4-configuration (700-750 cm^{-1}) is completely absent. The distribution of the monomer units has been investigated by ^{13}C-NMR spectroscopy, in analogy with other cationic isobutene-diene copolymers studied by us.

Fig. 2 shows the ^{13}C-NMR spectrum of the same sample shown in Fig. 1. Four regions are evident in Fig. 2. Between 130 and 140 ppm from TMS, there are three signals due to the unsaturated carbons of TMB. The assignments have been attributed following the scheme adopted for other copolymers of isobutene with symmetric dienes, i.e. butadiene (CORNO et al. 1979), 2,3-dimethyl-butadiene (CORNO et al. 1982) and 2,4-hexadiene (PRIOLA et al.).

We represent the TMB molecule in the copolymer chain as follows:

$- C(CH_3)_2 - C(1)H = C(2)H - C(CH_3)_2 -$

while the I unit arises from the normal head-to-tail addition $(-CH_2-C\ (CH_3)_2\ -)$.

The resonance of the two unsaturated carbons of the triad TTT occurs at 134.99 ppm from TMS where there is also the resonance of the same carbons of the triad ITT which, clearly, does not differ from the previous one for the position of the gem-dimethyl group. Conversely, triads TTI and ITI are different from the previous ones because the same group is shifted of one bond. According to the previous notations (CORNO at al. 1979) the two methyls pass from γ' to δ' position with respect to carbon - C(1)H = and from γ to δ position with respect to carbon - C(2)H =. As the value of γ and δ' is negative and that of γ' and δ is positive, there is a downfield shift $(-\ \gamma'\ +\ \delta')$ of the -C(2)H = resonance and an upfield shift $(-\gamma+\delta)$ of the resonance of carbon -C(1)H =. The ratio of the intensity of the signal at 134.99 ppm relative to that of the two signals at 138.57 and 131.47 corresponds to the ratio between the fractions of dyads TT and TI.

A second region of the spectrum is that between 60 and 48 ppm where there are peaks attributable to the methylene of isobutene. Four signals are evident. That occurring downfield (59.53 ppm) is due to the tetrads > III (the symbol > denotes either the unit I or T). The signal of the tetrads > TII occurs at 58.35 ppm which differ from the previous one for the absence of a second gem-dimethyl group in δ position. An upfield shift of about 8 ppm concerns with the signals of the tetrads > IIT, because of the presence of the dimethyl group in γ position, while the tetrads >TIT (which are different from the previous ones for the absence of the gem-dimethyl group in δ position) give rise to higher upfield shift. In practice, by measuring the intensity of the four signals of this region the fractions of the following triads III, IIT, TII and TIT can be obtained.

The third region of the spectrum, that ranking from 45 to 35 ppm, includes the signals due to quaternary carbons. The number of peaks is relevant and presently their complete attribution is not possible. The difficulty in assigning the signals of quaternary carbons in isobutene-based copolymers was previously discussed (PRIOLA et al.).

The last region of Fig. 2 includes the signals of methyls of both the monomers (32-20 ppm). Two bands, exhibiting fine structure, are evident.

The first, occurring between 31 and 30 ppm, is attributable to the methyls of gem-dimethyl groups separated by at least one methylene bridge.

The second band, observable between 23 and 22 ppm, is assigned to adjacent dimethyl groups.

By adopting the following notations:

$$-\underset{(1)}{\mathrm{C\ (CH_3)_2}} - \mathrm{CH = CH} - \underset{(2)}{\mathrm{C\ (CH_3)_2}} -$$

the first band will embrace the signals of the I methyls in the dyads II and TI and also the signal of the gem-dimethyl group (2) of the diene in the dyad TI.

The second band will include the signals of the I methyls in the dyad IT, of the dimethyl group (2) of the diene in the dyad TT and the signals of the dimethyl group (1) of the diene in both the dyads IT and TT.

^{13}C-NMR spectra permit the evaluation of the monomer distribution as from them the fractions of the triads centered on I and the fractions of the dyads are obtainable. The first series of values (of the triads) can be directly calculated from the area of signals of the I methylene, while the second series of values can be obtained as follows. The area of the peak observed between 23 and 22 ppm is divided by 2, because it arises from the contribution of two gem-dimethyl groups of the dyads IT and TT, as said above.

The area of the signal occurring between 31 and 30 ppm is due to the dyads II + TI, while half of the area of the signal between 23 and 22 ppm is due to the dyads IT + II. The ratio of the dyads TI (=IT) and TT is obtainable from the signals of the unsaturated carbons and hence, by subtracting the contribution of the dyad TI from the signal between 31 and 30 ppm, the value of the dyads II can be calculated.

Therefore the complete set of values pertaining to dyads II, IT+TI and TT is obtainable. Tab. II shows the fractions of sequences calculated for the samples of Tab. I which have been used for calculating the reactivity ratios of I and TMB (s. previous parag.).

CONCLUSIONS

The copolymerization of I with TMB has evidenced some interesting aspects concerning the reactivity of t-allyl carbenium ions present in the system which, in turn, influences the structure of the resulting copolymer. The value of the reactivity ratios of both the monomers indicates that the reactivity of TMB is high, although lesser than that of I. This fact agrees with the relatively high stability of the tert-allyl-

TABLE II. Dyad and triad fractions in I-TMB copolymers

Sample a)	1	2	3
II	0.554	0.470	0.259
IT + TI	0.401	0.428	0.514
TT	0.045	0.102	0.227
III	0.541	0.498	0.252
IIT + TII	0.336	0.338	0.387
TIT	0.123	0.164	0.361

a) The samples are described in Tab I

carbenium ion, i.e. $\sim CH = \overset{\oplus}{CH} = C\ (CH_3)_2$, derived from TMB monomer. The favourable energetic situation encountered in the TMB^+ ion, may account also the exclusive presence of the trans-1,4-TMB unit, while in the analogous copolymer based on HD (PRIOLA et al.) about 10-15% of 2,3-HD unit is observed (the diene active species in this case is $\sim CH = \overset{\oplus}{CH} = CHCH_3$). On the other hand, I gives rise to a t-carbenium ion which is more reactive than TMB ion and this fact may explain the higher reactivity of I with respect to TMB.

In conclusion, the steric hindrance existing in the TMB molecule, due to the presence of 4 methyl groups in the 1 and 4 positions, does neither inhibit the diene insertion in the copolymer chain nor induce a block-type monomer distribution.

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Received November 16, accepted November 23, 1982