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Identification of olefin end groups in commercial polybutene oligomers

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Summary

Olefin end groups in commercial polybutenes were assigned using model compound 2,3,4,6,6-pentamethylhept-2-ene and isobutylene oligomers formed through coupling reactions of chlorinated and non-chlorinated isobutylene dimers. The formation of these structures is discussed.

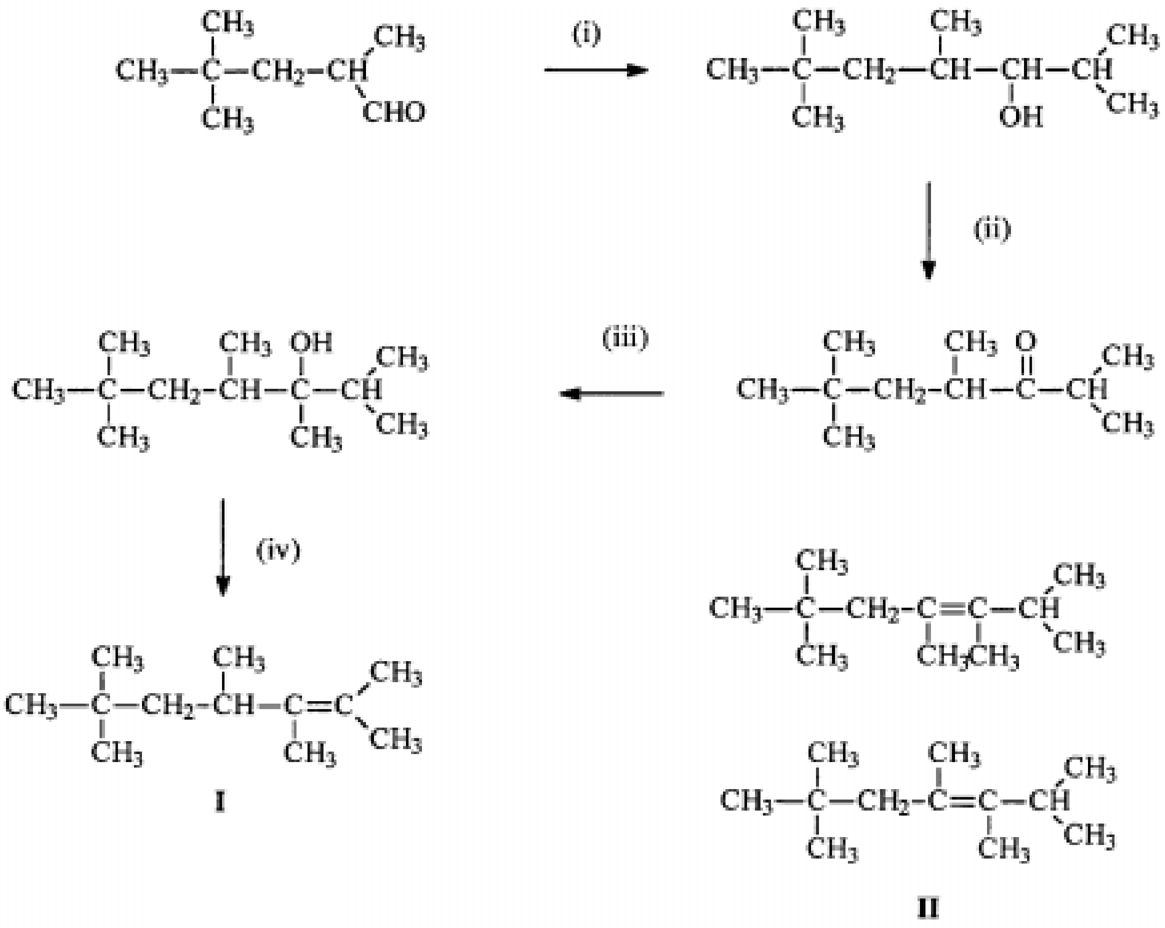
Introduction

Industrially produced polybutenes (PB) find uses in a vast number of applications from sealants and synthetic lubricants (1) to providing the hydrocarbon backbone for fuel and oil dispersants. Conventional polymerisation which uses chloro-aluminium or boron trifluoride type Lewis acids, produces low molecular weight polymers (M_n 500-6000) with a relatively broad molecular weight distribution (typically M_w/M_n 1.5-2). The backbones of these polybutenes are made predominantly of isobutylene units with only small contributions from the less reactive butenes in the C4 feed stream. Chain transfer is dominant in this type of polymerisation leaving olefin groups at the end of the polymer chain and a high catalyst turnover. Both of these factors are desirable in a commercial process. For additive applications in particular, the polymer end group structure is important as it dictates the ease with which derivitization occurs. For this reason the identity of these olefins is of interest. Analysis of commercial polybutenes by nuclear magnetic resonance spectroscopy (NMR) reveals a distribution of olefins which is largely dependent upon the Lewis acid catalyst used. Although most of the major end groups in PB have now been clearly identified (2-5), many of the minor structures remain unresolved. We describe the preparation of model compounds to aid the interpretation of some of these structures.

Experimental

Materials

Heptane was dried by distillation over sodium metal. EADC was purchased from Aldrich as a 1M ethylaluminium dichloride solution in hexanes. 2-Chloro-2,4,4-trimethylpentane was prepared by hydrochlorinating 2,4,4-trimethylpent-1-ene. Commercial polymers used were Ultravis 10 (Highly reactive) and Hyvis 10.



Scheme 1 (i) Pr^iMgBr in Et_2O at 0°C, 35°C 45 min., 2M H_2SO_4, 74% b.p. 116-128°C mm Hg (ii) CrO_3/Py in CH_2Cl_2, 15 min. RT., $NaHCO_3/H_2O$, 78% b.p. 111-113°C 90 mm Hg (iii) MeMgI in Et_2O at 0°C, 35°C 1hr., 2M H_2SO_4 0°C, 89.6%, b.p. 116-124 °C 41 mm Hg (iv) I_2 160°C 10 min., $Na_2S_2O_3/H_2O$ mixture of I (59% based on GC purity) and II, b.p. 145-155°C 488 mm Hg, preparative GC 97.3% (I).

Preparation of Model Compounds I and II

These model compounds were prepared according to Scheme 1. 2,4,4-Trimethylpentanal was obtained from 2,4,4-trimethylpent-1-ene using the method of Kennedy *et al* (6).

Analysis

NMR spectra were obtained using a Bruker AC 250 spectrometer. ^{13}C spectra were inverse gated decoupled and chromium (III) acetylacetonate was used as a relaxation agent. DEPT 135° and 90° experiments were also employed to determine carbon substitution.

Results and discussion

^{13} C NMR end group structure in PB

Commercially produced PB can be broadly divided by end group structure into two categories. Those that are termed highly reactive (HR) are generally prepared using

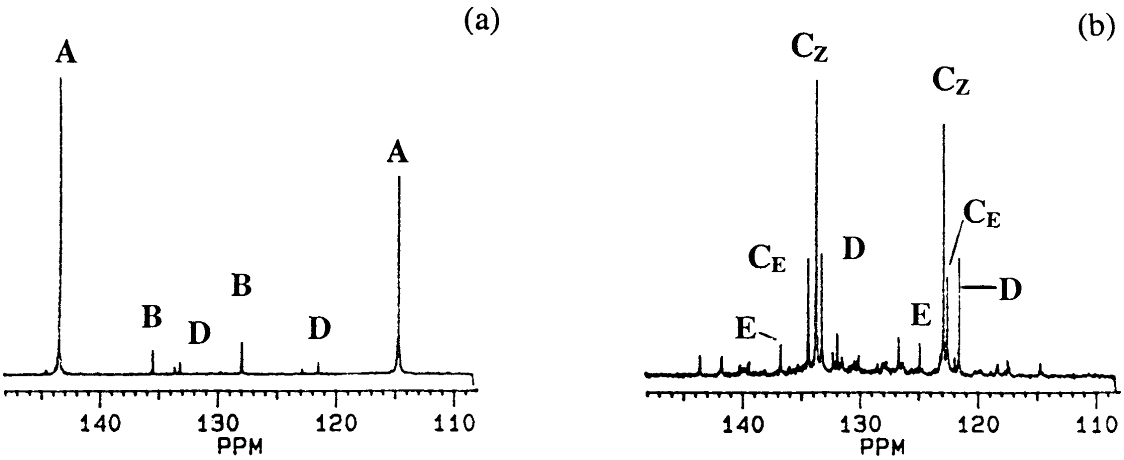


Figure 1 Olefin region of the ^{13}C NMR spectrum of polybutenes
(a) Ultravis 10 (b) Hyvis 10

boron trifluoride complexes as Lewis acids initiators (7). They consist predominantly of terminal vinylidene groups A and some tri-substituted olefin B (Figure 1a). The second category covers polybutenes produced with halides. The range of olefin end groups to be found in these polymers is larger and they contain far less of A and B. Instead, a number of other end group structures are observed in relatively high concentrations such as the tri-substituted isomers C_E and C_Z (2-4) with peaks at 134.2,122.3 and 133.8, 122.7 ppm (Figure 1b). Amongst the more intense peaks are those found at 133.1 and 121.5 ppm and these have recently been unambiguously identified as D. PB of this type also exhibit low intensity peaks at 136.5 and 124.5 (Figure 1b) and we have established through DEPT experiments that they belong to quaternary (quat.) carbons and hence to a tetra-substituted olefin. During the synthesis of 2,3,4,6,6-pentamethylhept-2-ene (I) which is a model compound for D we observed the formation of both I and II in the final elimination stage (Scheme 2). The isomers of II provide a suitable model compound for olefin end group E (Table 1). Examination of the ^{13}C NMR spectrum for II reveals chemical shifts at 136.4, 136.1 and 125.0, 124.9 ppm which are very similar to the chemical shifts observed in PB at

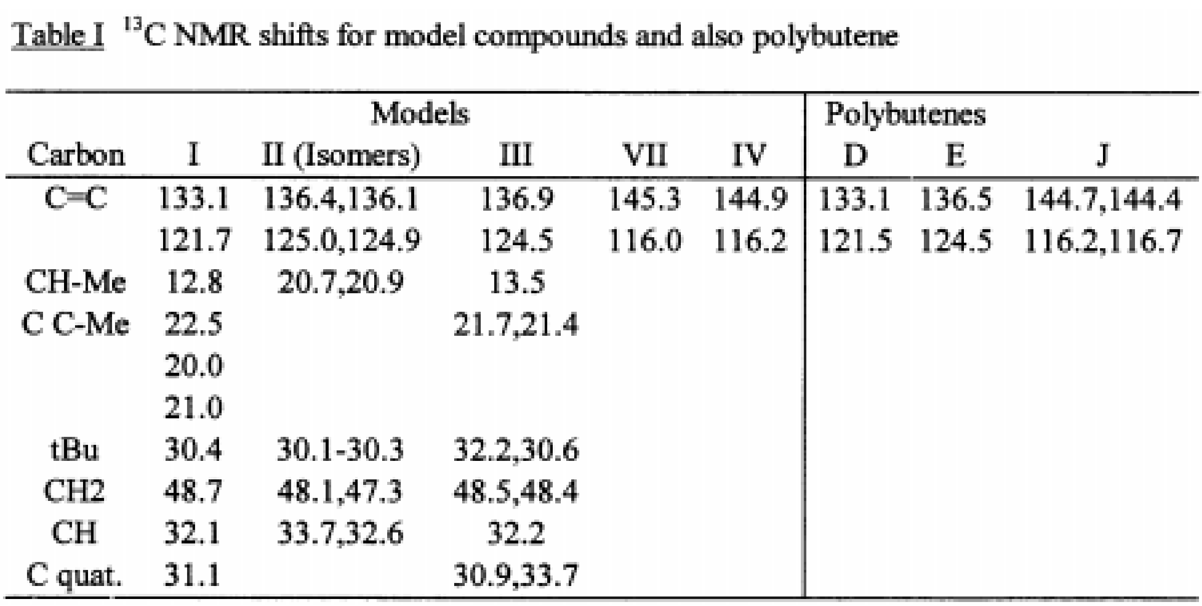
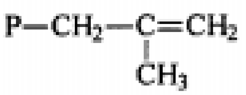


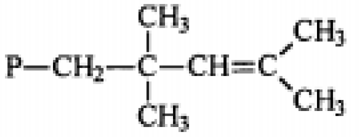
Table I ^{13}C NMR shifts for model compounds and also polybutene

	Models					Polybutenes		
Carbon	I	II (Isomers)	III	VII	IV	D	E	J
C=C	133.1	136.4,136.1	136.9	145.3	144.9	133.1	136.5	144.7,144.4
	121.7	125.0,124.9	124.5	116.0	116.2	121.5	124.5	116.2,116.7
CH-Me	12.8	20.7,20.9	13.5					
C C-Me	22.5		21.7,21.4					
	20.0							
	21.0							
tBu	30.4	30.1-30.3	32.2,30.6					
CH2	48.7	48.1,47.3	48.5,48.4					
CH	32.1	33.7,32.6	32.2					
C quat.	31.1		30.9,33.7					



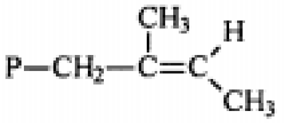
$P-CH_2-C(CH_3)=CH_2$

A



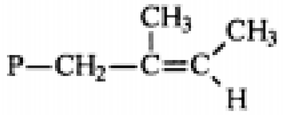
$P-CH_2-C(CH_3)_2-CH=C(CH_3)_2$

B



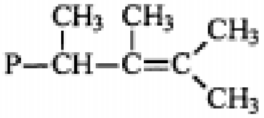
$P-CH_2-C(CH_3)=CH(CH_3)$

Cz



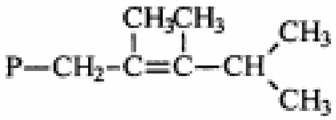
$P-CH_2-C(CH_3)=CH(CH_3)$

CE



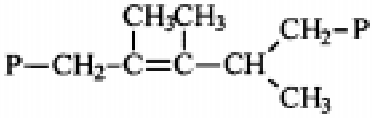
$P-CH(CH_3)-C(CH_3)=C(CH_3)_2$

D



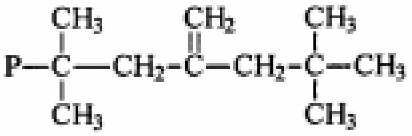
$P-CH_2-C(CH_3)=C(CH_3)-CH(CH_3)_2$

E



$P-CH_2-C(CH_3)=C(CH_3)-CH(CH_3)-CH_2-P$

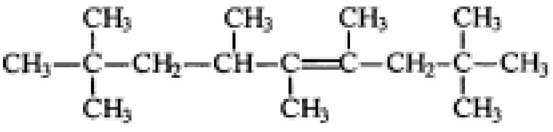
H



$P-C(CH_3)_2-CH_2-C(=CH_2)-CH_2-C(CH_3)_2-CH_3$

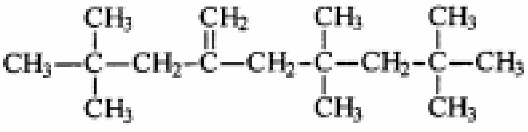
J

136.5 and 124.5. The low intensity peaks in PB are attributed to olefin E. It is interesting to note however, that only one isomer for E is observed in commercial PB and as yet reasons for this remain unexplained.



$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-C(CH_3)=C(CH_3)-CH_2-C(CH_3)_2-CH_3$

III



$CH_3-C(CH_3)_2-CH_2-C(=CH_2)-CH_2-C(CH_3)_2-CH_2-C(CH_3)_2-CH_3$

IV

Coupling Experiments

It is understood that in the absence of polymerisation, isobutylene oligomers subjected to Lewis acid catalysts may undergo a number of reactions which include polymer cracking and coupling (8-11). Experiments using isobutylene dimers and ethylaluminium dichloride at ambient temperatures have been described by Hasegawa and Higashimura (8). These workers found the product to be a mixture of oligomers as a result of both coupling and cracking reactions but did not identify the main structures. We decided to carry out these reactions at low temperatures to establish whether these model products might be used to assist in the characterisation of the minor olefin groups found in commercial polybutenes. 2,4,4-Trimethylpent-1-ene and 2-chloro-2,4,4-trimethylpentane were treated with EADC at 0°C and -60°C and the product analysed by ^{13}C NMR and GC. At -60°C both coupling and cracking occurs as indicated by the GC analysis (Figure 2a) which shows predominantly tetramers and trimers. Examination of the ^{13}C NMR spectrum of the mixture (Figure 3a) reveals two main olefin peaks at 124.5 and 136.9 ppm and these were found to be quaternary carbons through a DEPT experiment. We believe the major product in these reactions to be the tetramer with structure III because of the similarity between double bond chemical shifts of the tetramer and those of model compound II (Table I). A methine

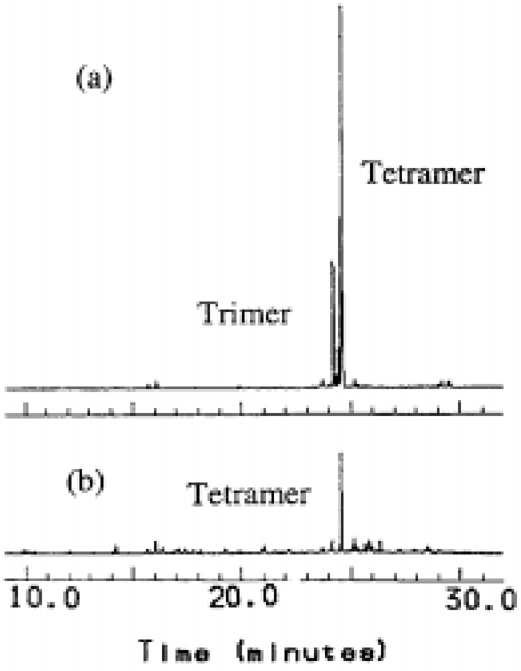


Figure 2 GC of product from coupling reactions of isobutylene dimers, 2,4,4-trimethylpent-1-ene (63 mmol) 2-chloro-2,4,4-trimethylpentane (5.2 mmol) EADC (5 mmol) stirred in heptane 1 hr
(a) -60°C (b) 0°C

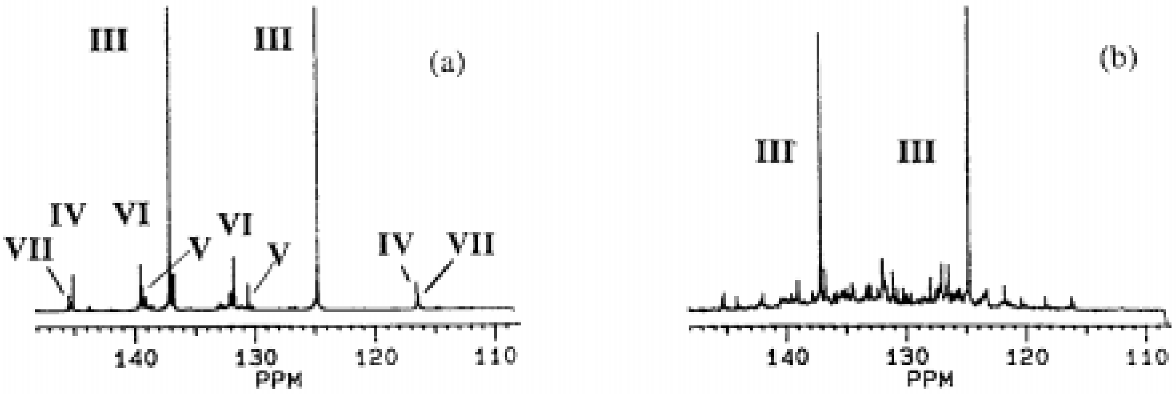
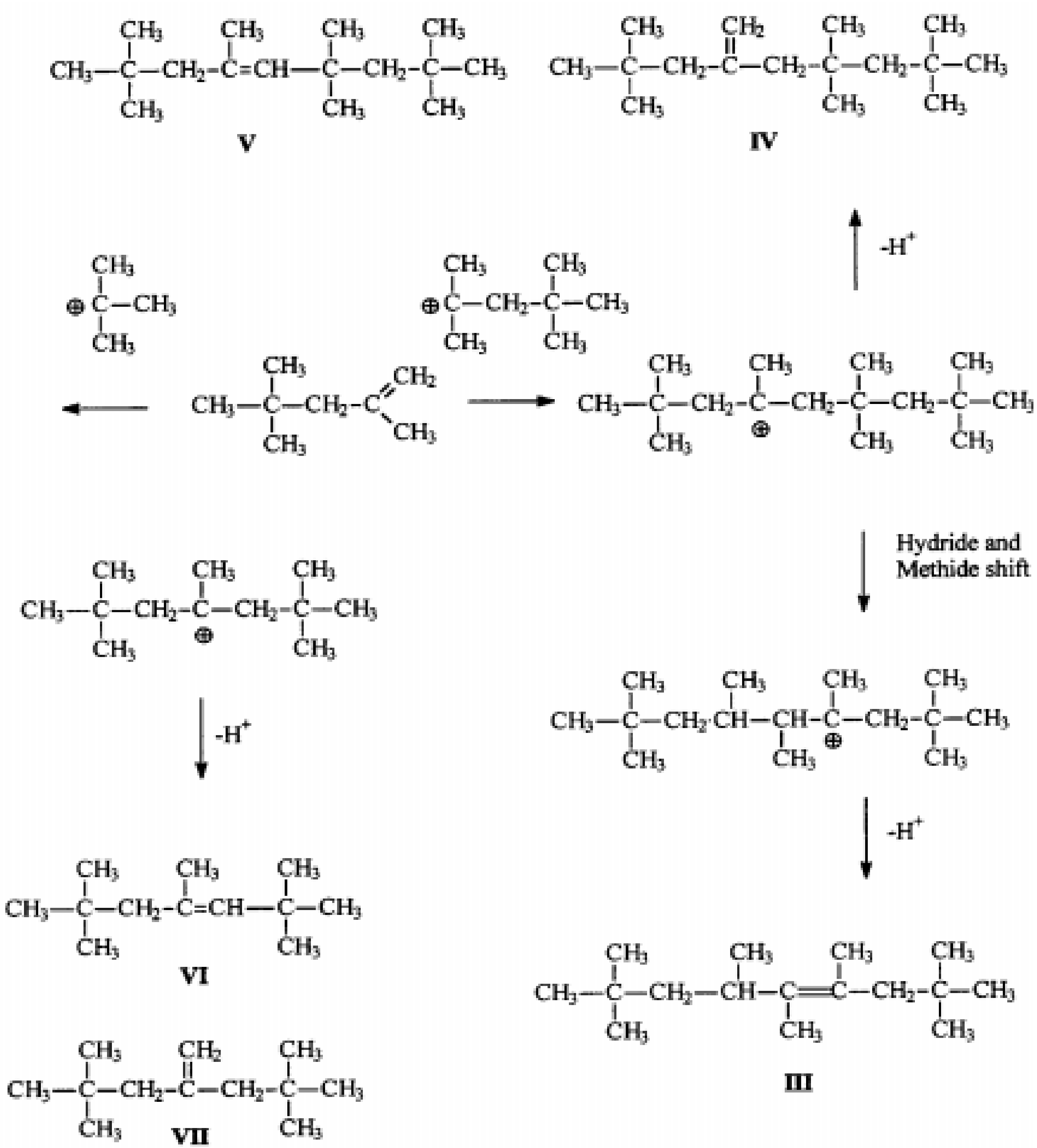


Figure 3 ^{13}C NMR spectrum of product from coupling reaction carried out at
(a) -60°C (b) 0°C

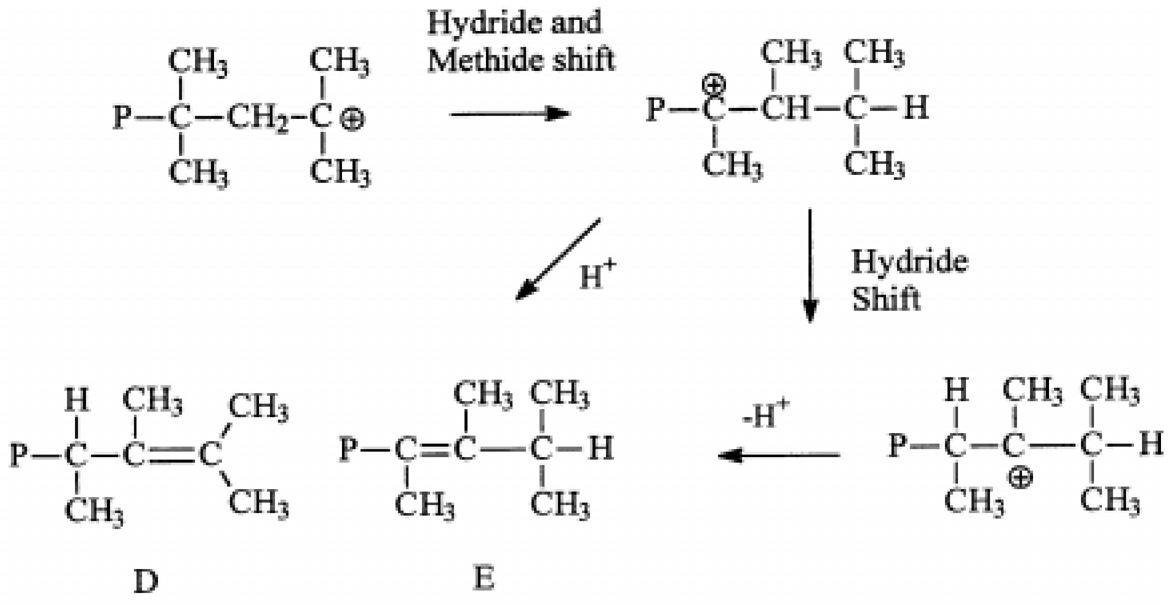
proton at 2.82 ppm is also found in the ^{1}H NMR spectrum and is consistent with a structure such as III. The formation of this olefin is likely to proceed through a hydride and methide shift prior to elimination as outlined in Scheme 2. The mixture contains additional peaks in the olefin region of the spectrum corresponding to tetramers IV (116.2 $\underline{CH}_2$, 144.9 quat.) and V (130.3 quat., 139.3 $\underline{CH}$). These were identified using literature values (8) and are seen to be derived from simple proton loss from the carbenium ion prior to rearrangement. The trimers VI (131.5 quat., 139.5 $\underline{CH}$) and VII (116.0 $\underline{CH}_2$, 145.3 quat.) were also present, identified by the chemical shifts (12) and their appearance can be explained through coupling of a t-butyl carbenium ion and 2,4,4-trimethylpent-1-ene. Coupling reactions of this type have also been described with isobutylene trimers which lose a t-butyl carbenium ion and undergo subsequent coupling reactions to form tetramers (13).



Scheme 2

When this reaction is carried out at the higher temperature of 0°C, the major product can still be attributed to III but the ^{13}C NMR spectrum shows far more complexity in the olefin region (Figure 3b). The isobutylene tetramers and trimers (IV-VII) are barely distinguishable above the many low intensity peaks (Figure 3b). Likewise the GC also shows a higher proportion of minor product (Figure 2b). These effects are most certainly the result of more cracking and coupling to higher oligomers. The significance of temperature in coupling experiments was also reported by Coca and Faust (14) during the coupling reaction of polyisobutylene catalysed with triffic acid. These workers found a reduction in cracking when going to lower temperatures.

The possibility that the double bond observed at 124.5 and 136.5 in commercial PB is an internal one such as H due to coupling between oligomer groups, cannot be excluded based on ^{13}C nmr results alone. The substituent effects upon the olefin significantly diminish after more than 3 carbons (15) so that major differences between the chemical shift of the tetramer double bond in III and that of H would not be expected. However, it is unlikely that significant amounts of H would be formed in PB through coupling of oligomers since coupling, being less favourable than polymerisation in terms of monomer reactivity, might only occur when the concentration of isobutylene was very low. It is more reasonable to expect that a terminal E structure is formed in PB through rearrangement of the carbenium ion. A route such as that suggested in Scheme 3 would account for both D and E.



Scheme 3

In highly reactive polybutene material minor peaks associated with the vinylidene region were also observed at 144.4 (quat.), 116.7 (CH_2) and 144.7 (quat.), 116.2 (CH_2). A DEPT experiment was used to establish the substitution of these olefin carbons (Figure 4). Table 1 highlights the change in chemical shift going from trimer VII to tetramer IV and the peaks observed in the HR PB are consistent with this type of structure. The tetramer IV provides a useful model for internal vinylidene and structure J is suggested to account for the low intensity peaks at 144.7 and 116.2. This olefin has already been identified in the proton NMR spectrum for PB prepared with BF_3 water complex (16). We observe more than one type of internal vinylidene and it is as yet unclear how they are formed.

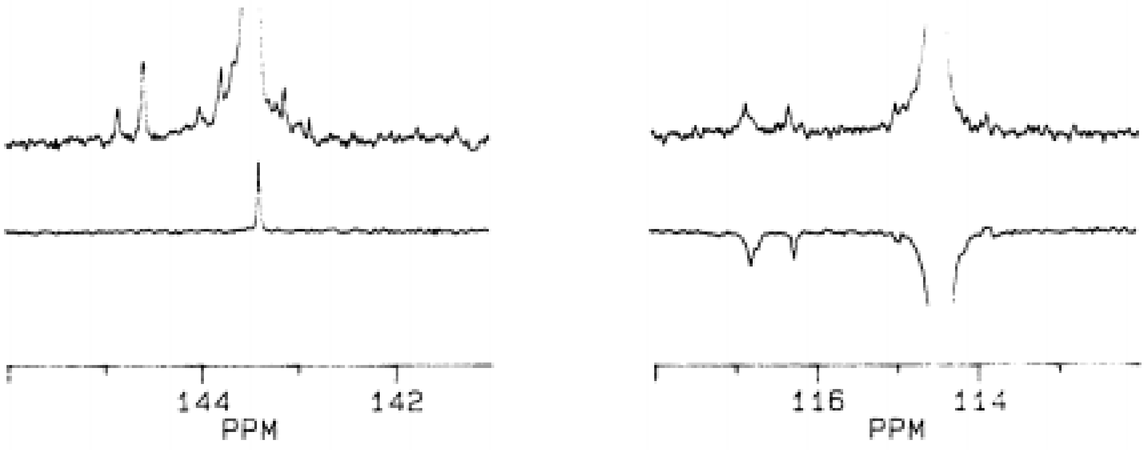


Figure 4 ^{13}C NMR spectra and DEPT 135° showing internal vinylidene in HR polybutene

References

1. Fotheringham JD, Polybutenes. In Shubkin R and Rudnick L (ed) Synthetic lubricants and high-performance fluids (2nd Ed Chem & Ind Series Vol 77)
2. Gunther W, Maenz K, Stadermann D (1995) Angew Chem Int Ed Eng 71: 234
3. Spevacek J, Toman L, Vlcek P (1995) Polym. Bull 34:
4. Wollenburg KF, Kolp CJ (1997) 213th ACS National Meeting Poly-441
5. Jamois D Tessier M Marechal E (1993) J Polym. Sci (Part A Poly Chem) 31:1923
6. Kennedy JP, Chang VSC and Francik WP (1982) J Polym Sci 20: 2809
7. Samson JNR BP Chemicals WO 85/01942 9th May 1985, Eaton BE Amoco Corporation US5,068,490 Nov. 26th 1991; Rath HP BASF Aktiengesellschaft US 5,408.018 April 18th 1995
8. Hasegawa H, Higashimura T, (1982) J App Polym. Sci 27: 171
9. Khalafov FR, Novrusova FA, Krentsel BA, Agaeva EA, Yafarov OI, Mekhtiev, SA,Kuhev AM, Nurullaev GG (1992) Acta Polym. 43:102
10. Khalafov FR, Novrusova FA, Ismailov EG, Krentsel BA (1990) Acta Polym 41(4): 226
11. Puskas I, Meyerson S (1984) J Org Chem 49: 258
12. Higashimura T, Miyoshi Y (1983) J App Polym. Sci 28: 241
13. Kennedy JP, Rengachary S (1974) S Adv Polym. Sci 14:1
14. Coca S, Faust R (1997) Macromol 30: 649
15. Dorman DE, Jautelat M, Roberts JD (1971) J Org Chem 36: 2757
16. Puskas I, Banas EM, Nerheim AG (1976) J Polym Sci 56:191