polymer communications

Double-bond-shift reactions in polymers made by ring-opening polymerization of cycloalkenes initiated by metathesis catalysts

K. J. Ivin, G. Łapienis* and J. J. Rooney
Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, UK
(Received 22 December 1979)

In a recent paper[1] we reported that the ring-opening polymerization of cyclopentene in the presence of cyclohexene gave, under certain conditions ($EtAlCl_2/WCl_6 \geqslant 10$), a product whose ^{13}C n.m.r. spectrum indicated the presence of $=CH(CH_2)_4CH=$ units, apparently formed by the copolymerization of cyclohexene. Blank experiments appeared to indicate the absence of a double-bond-shift reaction. We have now found that such experiments can be misleading if carried out with $EtAlCl_2/WCl_6$ ratios in the vicinity of 10, probably because of sensitivity to impurities and to the method of mixing.

When cyclopentene is polymerized with $EtAlCl_2/WCl_6$ (20/1), the $EtAlCl_2$ being added last, the product always has a spectrum of the type shown in *Figure 1* of ref 1. The peaks at 130.06, 32.80 and 27.45 ppm are in the positions expected for $=CH(CH_2)_2CH=$ units, as observed in 1,4-polybutadiene[2]. The peaks at 130.54, 130.19, 32.54, 29.21 and 27.14 ppm may still be assigned to $=CH(CH_2)_4CH=$ units (*Table 1*). The intensities indicate, as expected, that $=CH(CH_2)_2CH=$ and $=CH(CH_2)_4CH=$ units are formed in comparable amounts and it was confirmed by g.l.c. of the volatile products that less than 1.5% of the latter is expelled as cyclohexene.

These results show clearly that a copolymer-type structure may be produced by homopolymerization of cyclopentene with a concomitant or subsequent double-bond-shift reaction. Further experiments showed that the double-bond-shift reaction was:

(a) a secondary reaction (Al/W = 26), increasing with time and reaching a limit corresponding to approximately 60% C_5, 20% C_4, 20% C_6 units (C_3 units may also sometimes be detected; see results for cyclooctadiene);

(b) less pronounced when WCl_6 and $EtAlCl_2$ were premixed and the monomer added last;

(c) suppressed by the addition of pyridine (Al/W/pyr = 20/1/2).

Attempts to detect genuine copolymerization by reaction of cyclopentene with cyclohexene-3,3,6,6-d_4 or 4-methylcyclohexene met with failure.

As an extension to this work we have examined the polymers produced from *cis,cis*-cycloocta-1,5-diene, initiated by R_4Sn/WCl_6 (R = phenyl, n-butyl, allyl) and $EtAlCl_2/WCl_6$ in chlorobenzene as solvent. The former catalyst systems are moderately active (10% yield/4 min), give a polymer with a high *cis* content (85%), and never show any sign of secondary *cis*/*trans* isomerization (as indicated by the total absence of a *tt* peak at 130.04 ppm; see *Table 1*). $EtAlCl_2/WCl_6$ is a much more active catalyst and can give three types of polymer according to the conditions.

Table 1 ^{13}C chemical shifts (±0.04 ppm) for $=CH(CH_2)_nCH=$ units in linear polyenes. Solvent, $CDCl_3$; referred to TMS. Compare ref 9

	CH=CH		α-CH_2[a]			
n	*trans*	*cis*	*trans*	*cis*	β-CH_2	γ-CH_2
1	128.90[b]	130.75[b]	35.64	30.51		
2[c]	130.15 (*tc*)[d] 130.04 (*tt*)	129.63 (*cc*) 129.46 (*ct*)	32.71	27.45		
3	130.32	129.85	32.19 (*tc*) 32.06 (*tt*)	26.90 (*cc*) 26.76 (*ct*)	29.84 (*cc*) 29.73 (*ct*) 29.56 (*tt*)	
4	130.54	130.19	32.54	27.14	29.21	
5	130.37	129.89	32.62	27.27	29.69 (*c*) 29.61 (*t*)	29.04 (*cc*) 28.91 (*ct*) 28.78 (*tt*)
6	130.37	129.89	32.62	27.27	29.78 (*c*) 29.65 (*t*)	29.26 (*c*) 29.09 (*t*)

[a] Three peaks (*tt, tc, cc*) would be expected for *n* = 1; only two peaks, separated by 5.1 ppm, are seen

[b] Note reversed line order compared with *n* = 2–6; assignment based on relative intensities compared with those of the α-CH_2 peaks

[c] Positions given in ref 2 are 0.76 ppm lower owing to different operating conditions

[d] *tc* denotes that the nearest double bond is *trans* and the next nearest is *cis*

---

* On leave from Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Łódź, Poland

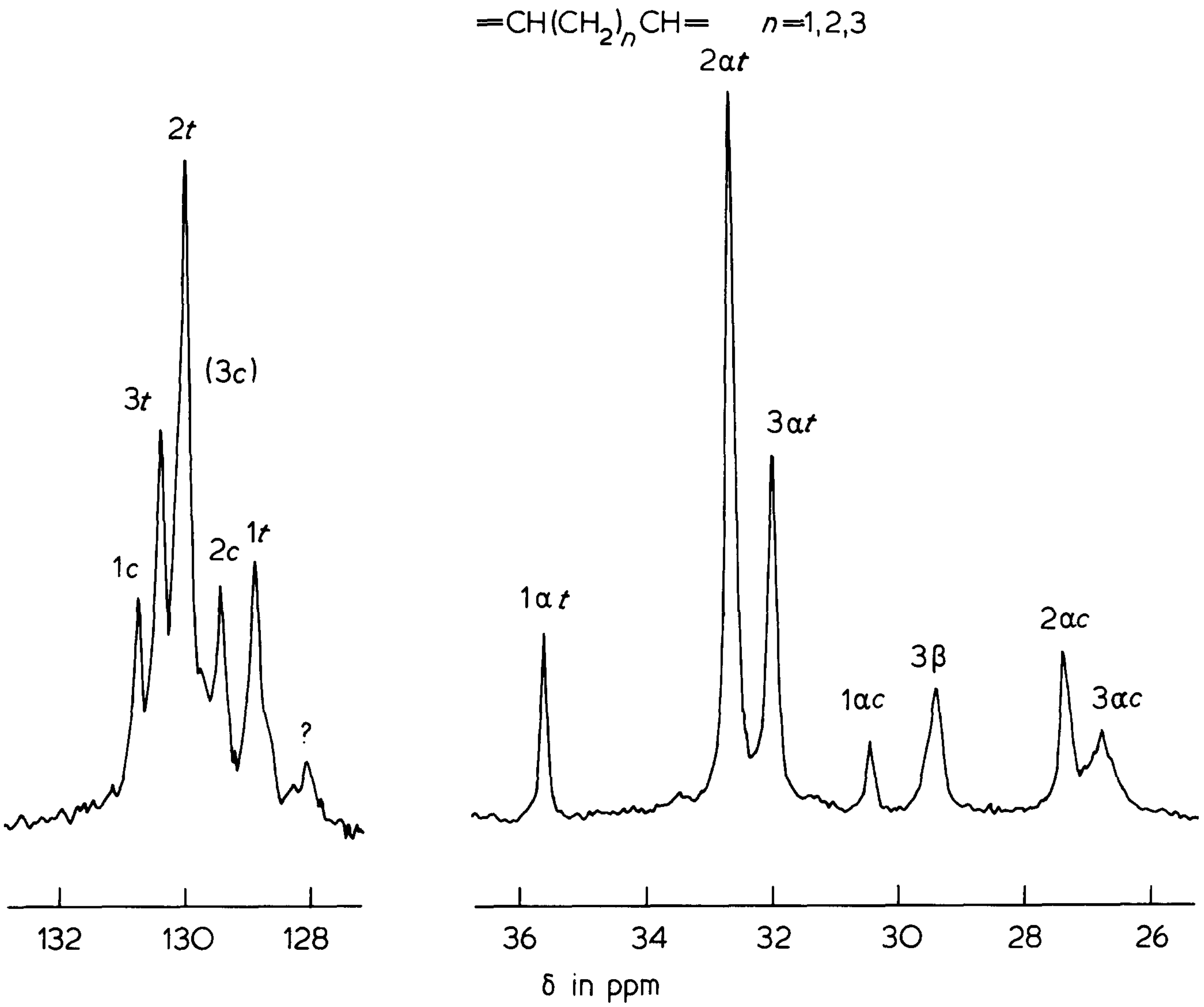


Figure 1 ^{13}C- ^{1}H n.m.r. spectrum of ring-opened polymer of cycloocta-1,5-diene which has undergone a double-bond-shift reaction (see text). The numbers above the peaks refer to the number n of CH_2 groups in the unit =CH(CH$_2$)$_n$CH=. For details see *Table 1*

(a) With Al/W = 4, and adding the monomer last, the reaction is moderately fast (34% yield/40 s) and gives clean ring-opening polymerization (with no sign of *tt* structures) and a high *cis* content (80%).

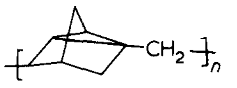
(b) With Al/W = 10, and again adding the monomer last, the reaction is faster (82% yield/5 s) and complete randomization of *cis* (55%)/*trans* (45%) double bonds is achieved as a result of secondary *cis*/*trans* isomerization of the preformed *cis* double bonds (one for each monomer unit).

(c) With Al/W = 20, and $EtAlCl_2$ added last, the reaction is fast (85%/30 s) and gives a polymer in which both *cis*/*trans* and double-bond-shift isomerizations have occurred. *Figure 1* shows the spectrum of a polymer in which the latter has proceeded to its maximum observed extent (approximately 54% C_4, 23% C_5 and 23% C_3 units). The peaks of the C_5 units are readily identified by comparison with a spectrum of the polymer of cyclopentene, while the peaks at 130.75, 128.90, 35.64 and 30.51 ppm are assigned to the complementary C_3 units (*Table 1*).

Double-bond-shift reactions have previously been shown to accompany the metathesis reactions of undec-1-ene[3], oct-1-ene[3] and pent-1-ene[4,5] under certain conditions, but this is the first clear demonstration of the effect in polyenes, apart from a brief report on 1,4-polybutadiene[6].

The mechanisms of the *cis*/*trans* isomerization and double-bond-shift reactions are not entirely clear. The former may occur as a secondary metathesis reaction once the metathesis sites become available as a result of consumption of the more strongly coordinating monomer molecules. It may also occur via a reversible hydrogen transfer reaction involving either $[W]^{\delta-}$–$H^{\delta+}$ or some other protonic species produced in the presence of excess $EtAlCl_2$. The double-bond-shift reaction is definitely catalysed by protonic species but whether this occurs at or away from the tungsten sites if not clear. The influence of the small amount of pyridine in suppressing this reaction should be noted.

We have observed that the cationic polymerization of 5-methylenenorbornene to give I:



previously demonstrated with $EtAlCl_2$ alone as catalyst[8], also occurs with all these metathesis catalysts, even in the presence of pyridine ($WCl_6/(CH_3)_4Sn$/pyr = 1/2/4). Thus sensitivity of double bond reactions to protonic catalysis may cover a very wide range of acid strength, depending upon the basicity of the substrate olefin. The formation of I accompanied by little or no ring-opening of 5-methylene-norbornene also indicates that any hydride or alkyl ligands are almost certainly polarized in the direction $[W]^{\delta-}-R^{\delta+}$, the tungsten ion being electron poor and drawing electron density away from the ligand R.

The ^{13}C n.m.r. positions characterizing the various types of $=CH(CH_2)_nCH=$ units are summarized in *Table 1*.

Acknowledgement

We thank SRC for financial support.

References

1 Ivin, K. J., Łapienis, G., Rooney, J. J. and Stewart, C. D. *Polymer* 1979, **20**, 1308
2 Elgert, K. F., Stützel, B., Frenzel, P., Cantow, H. J. and Streck, R. *Makromol. Chem.* 1973, **170**, 257
3 Hummel, K. and Ast, W. *Naturwiss.* 1970, **57**, 245
4 Uchida, Y., Hidai, M. and Tatsumi, T. *Bull. Chem. Soc. Japan* 1972, **45**, 1158
5 Uchida, A., Kobayashi, K. and Matsuda, S. *Ind. Eng. Chem. Prod. Res. Develop.* 1972, **11**, 389
6 Dall'Asta, G., Stigliani, G., Greco, A. and Motta, L. *Polym. Prepr.* 1972, **13**, 910
7 Ivin, K. J., Reddy, B. S. R. and Rooney, J. J. Unpublished results
8 Kennedy, J. P. and Makowski, H. S. *J. Macromol. Sci. (Chem)* 1967, **A1**, 345
9 Chen, H. Y. *Polym. Prepr.* 1976, **17**, 688

Synthesis of novel siloxane block copolymers for use in photophysical studies

Miecheslaw Mazurek*, Alastair M. North and Richard A. Pethrick
Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde,
295 Cathedral Street, Glasgow G1 1XL, UK
(Received 9 December 1979)

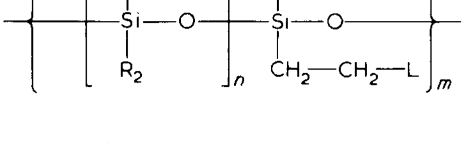
Introduction

In vivo chlorophyll (Chla) is tightly bound to natural proteins[1,2]. This forms so-called 'antenna chlorophyll' which allows efficient energy transfer to the active centre necessary for photosynthesis[1]. The concentration of chlorophyll in chloroplast is high, typically 0.1 M. Lower concentrations of Chla in solution exhibit strong quenching of fluorescence although in the absence of photoreactive centres, or at high dilution, Chla fluorescence can be intense. It has been proposed that the high activity of Chla in choroplasts is associated with a specific and regular organization of the Chla molecules induced by complexing to the protein. Attempts to model chloroplast activity in synthetic polymer systems must then include a photon collection and energy concentration facility corresponding to that exhibited by the Chla–protein–lipid combination, and it is as part progress to this objective that the syntheses described herein are directed.

A number of recent papers[3–9] describe the effect of polymeric species on the energy transfer characteristics of Chla solutions. The polymer used, poly(vinyl pyridine), interacts with the chlorophyll in a non-specific manner leading to a statistical distribution of non-oriented interacting sites along the polymer backbone and to little energy collection advantage. It is clear from these studies that use of a block copolymer with regularly spaced single interacting sites might offer a clear analogue to the *in vivo* collection and concentration system.

Regular or block copolymers can be synthesized by the anionic polymerization of vinyl monomers in the presence of difunctional reagents, usually dihaloalkanes. However, such syntheses do not lend themselves to the regular spacing of functional activity desired in this case. An alternative can be found in the condensation polymerization of siloxane derivates.

In this paper, the synthesis of a series of polymers with pendant groups capable of interacting with Chla is described. The polymers conform to the general structure:



$$\left[\left[-\overset{R_1}{\underset{R_2}{\mathrm{Si}}}-\mathrm{O}-\right]_n-\overset{R_3}{\underset{CH_2-CH_2-L}{\mathrm{Si}}}-\mathrm{O}-\right]_m$$

where L is a complexing ligand, separated by 'spacers' of different known lengths. The synthesis is achieved by the heterofunctional condensation of α,ω-difunctional (hydroxy or alkoxy functionality) siloxane oligomers with a difunctional silane containing the ligand groups attached to a silicon atom by means of an ethylene bridge. The critical step is the hydrosilation of the ligand–vinyl derivative:

---

* Permanent address: Institute for Molecular and Macromolecular Sciences, Polish Academy of Sciences, Łodz, Poland