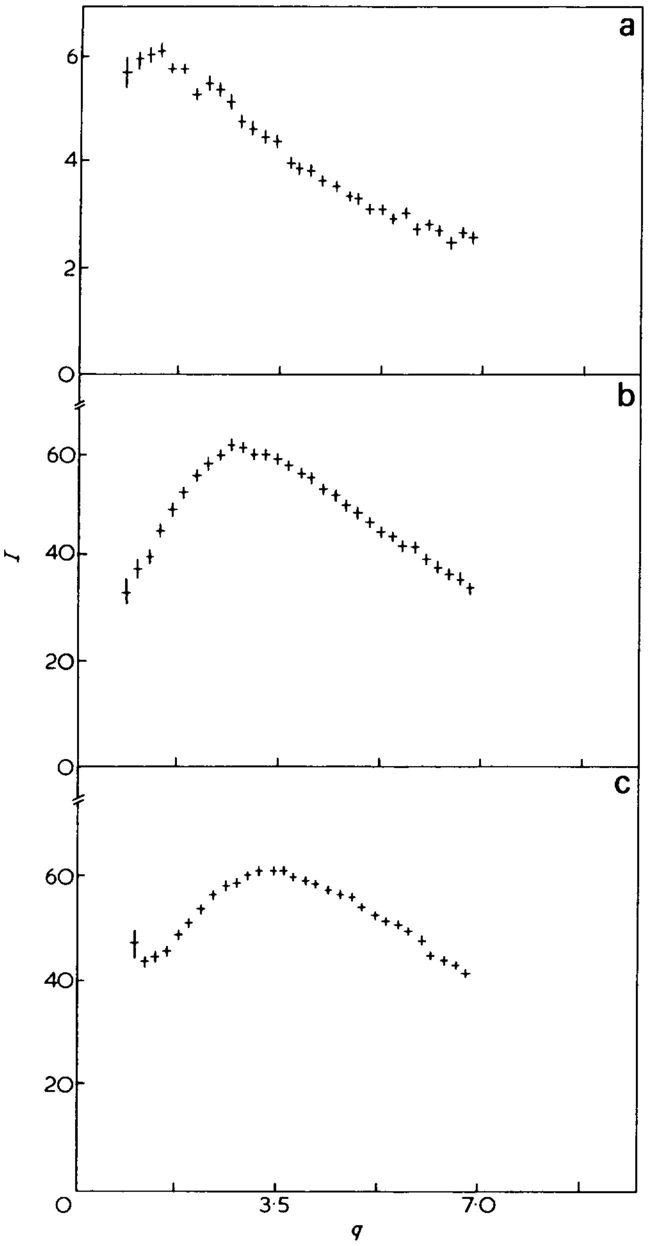


Figure 1 Scattering distribution function obtained with CS_2 solution (a) 1%, (b) 20%, and solid state (c).

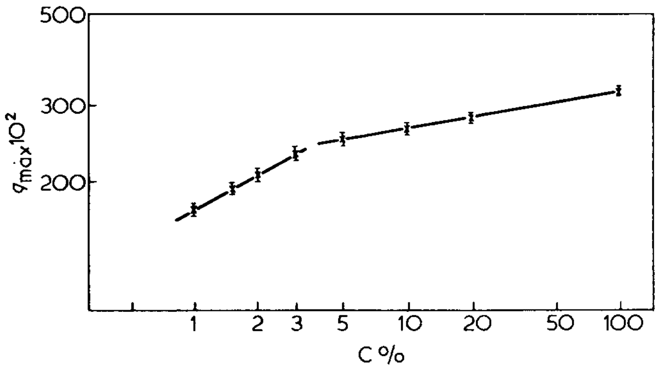


Figure 2 Concentration dependence of q_{max}.

The scattering curve obtained in the bulk could be interpreted in terms of correlation hole [3,4]. Using the theoretical prediction of these references we have shown[5] that there is good agreement between experimental and theoretical values calculated by introducing the ratio between labelled and non labelled sequences.

The hypothesis of the previous theoretical treatment is only applicable in the case of the melted polymer, thus it is now impossible to use it in solution, especially in dilute solutions. However work is being done to extend the field of validity of the theory to the semi dilute regime. This will be the aim of a subsequent paper where more extensive experimental results and their theoretical justification will be given.

References

1 Kirste, R.G., Kruse, W.A. and Schetten, J. *Makromol Chem* 1972, **162**, 299
2 Cotton, J.P. *et al. Macromolecules*, 1974, 7, 863
3 Daoud, M. *et al. Macromolecules*, 1975, 8, 804
4 de Gennes, P.G. *J de Physique*, 1970, 31, 235
5 Cotton, J.P. *et al., I.A.E.A.* Vienna, Vol. 1, 563 (1978).

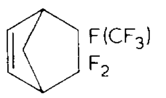
Ring-opening polymerization of fluorine substituted bicyclo[2,2,1] hept-2-enes and -hepta-2,5-dienes

W.J. Feast and B. Wilson
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE

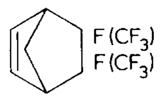
The production of poly(1-pentenylenes), linear hydrocarbon elastomers, by the ring opening polymerization of cyclopentene is well established.[1] The work reported here stemmed from an attempt to extend this reaction to the polymerization of 1H, 2H-hexafluorocyclopentene prompted by the hope that the resultant polymers would combine the low glass transition temperatures associated with polypentenylenes, with the thermal stability and solvent resistance associated with fluorocarbon polymers. This attempt was unsuccessful but raised the question of the polymerizability of fluorinated monomers by typical metathesis polymerization catalysts. A variety of monomers containing electron-withdrawing substituents have been reported to undergo ring-opening polymerization in the presence of typical metathesis catalysts[2–6] but the only examples of possible metathesis reactions of fluorinated systems known to us are the cyclobutane-diene interconversions described by Gassman and Johnson.[7]

We now report that the monomers I → VI are readily polymerized and copolymerized by ring opening at the unsubstituted double bond under the influence of a variety of metathesis catalysts derived from tungsten

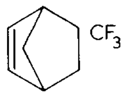
0032-3861/79/101182-02$02.00



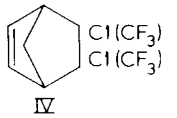
I



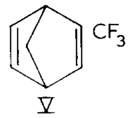
II



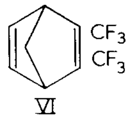
III



IV



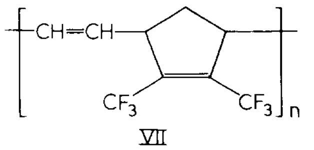
V



VI

hexachloride. In all these examples the fluorine substituents are remote from the double bond which participates in the reaction and in this respect our observations parallel those reported by Overberger and co-workers for the Ziegler-Natta polymerization of trifluoromethyl-substituted alkenes; they found that successful polymerization required that the CF_3-group was at least one carbon atom removed from the double bond [8].

In this work standard dry-box and vacuum line techniques were used; in a typical reaction the glass reaction vessel was charged with tetraphenyltin, evacuated and then filled with an atmosphere of dry nitrogen; a solution of tungsten hexachloride in dry toluene was then introduced by injection through a serum cap using an air-tight syringe, and the mixture was stirred vigorously for 12–15 min during which time the colour changed from blue-black to a dark red-brown. The dried, degassed monomer was injected into the active catalyst system using an air-tight syringe, and after an appropriate time the reaction was terminated by addition of methanol. Product polymers were recovered by precipitation from an appropriate solvent/non-solvent combination. For example, 2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta-2,5-diene (VI) was polymerized in this manner, using a monomer: Sn:W ratio of 400:2:1 to give, after 30 min at *ca.* 20°C, poly(4,5-bis(trifluoromethyl)-1, 3-cyclopentenylene vinylene) (VII) in 70% yield. The polymer had an intrinsic viscosity $[\eta] = 0.50$ dl/g (MEK at $25.00 \pm 0.01°$) and satisfactory C, H and F elemental analyses.



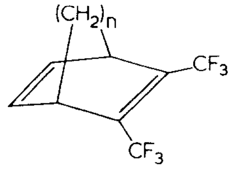
VII

The structures of the product polymers were established by i.r., ^{1}H, ^{19}F and ^{13}C n.m.r. spectroscopy, ^{13}C n.m.r. proving particularly useful. For example, polymer VII above displayed well-resolved resonances in the vinylic, methine and methylene regions of the ^{13}C spectrum which could be assigned to repeat units in which the vinylene units had either *cis* or *trans* geometry; the integrated intensity ratios of the separate resonances in each region of the spectrum were reasonably internally consistent, indicating respectively, 56, 52 and 53% of *cis* double bonds along the main chain.

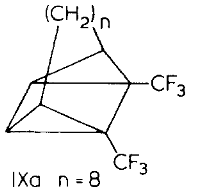
Of the monomers listed above the dienes V and VI were the most readily polymerized. Several catalyst systems derived from tungsten hexachloride were investigated and, in addition to tetraphenyltin, trialkylaluminiums and dialkylaluminium chlorides either with or without oxygenated promoters such as Na_2O_2 were shown to be effective co-catalysts. Indeed for the most reactive monomer, VI, an exothermic ring-opening polymerization was effected by tungsten hexachloride in toluene without any added co-catalyst or promoter.

Most of the polymers, and co-polymers with cyclopentene, derived from monomers I → VI could be cast as films from solution; solubilities ranged from methanol soluble/toluene insoluble (polymer derived from I) to toluene soluble/methanol insoluble (polymer VII); glass transition temperatures ranged from 267 K (2:1 co-polymer of VI with cyclopentene) to 437 → 448 K (homopolymer from I, value depending on the endo/exo-isomer distribution in the monomer).

The mechanism of metathesis polymerization is currently believed to involve a metallo-cyclobutane formed by reaction between a metallocarbene and a coordinated olefin [9] earlier proposed mechanisms have included a 'quasi cyclobutane' transition state, and the intermediacy of metallo-cyclopentanes. The results of Gassman and Johnson are the main evidence supporting the possible involvement of cyclobutanes in metathesis [7];they observed a diene to cyclobutane conversion for compound VIIIa and cyclobutane to diene conversions for compounds IXb and IXc the interconversions being catalysed by 'an accepted metathesis catalyst $PhWCl_3/AlCl_3$'. These authors also reported that the bicyclic dienes VIIIb and VI were unaffected by their catalyst although it retained its activity for the cyclobutane-diene interconversion even after 'normal metathesis activity' had been quenched by the addition of Michael acceptors. Our observation that bicyclic diene VI is particularly susceptible to ring opening polymerization by a range of metathesis catalysts and is even polymerized by pure tungsten hexachloride contrasts with its reported lack of reactivity with the $PhWCl_3/AlCl_3$ catalyst and suggests that the interesting cyclobutane-diene interconversions observed with this catalyst have little relevance to the mechanism of the generality of matethesis polymerizations.



VIIIa n = 8
VIIIb n = 2
VI n = 1



IXa n = 8
IXb n = 2
IXc n = 1

References

1 Dall'Asta, G. *Rubber Chem Technol,* 1974, **47(3),** 511
2 Ofstead, E.A. U.S. Patent 3,597,403 (1969)
3 Ofstead, E.A. *4th Int Synth Rubber Symp,* 1969, **2,** 42
4 Hepworth, P. Ger. Offen, 2,231,995 (1973).
5 T. Ueshima, S. Kobayashi and M. Matsuaka, Ger Offen, 2,316,087 (1973)
6 Ueshima, T. and Kobayashi, S. *Jn Plastics* 1974, **24,** 11
7 Gassman, P.G. and Johnson, T.H. *J Amer Chem Soc* 1976, **98,** 861 and references therein
8 Overberger, C.G. and Davidson, E.B. *J Polym Sci,* 1962, **62,** 23; and Overgerger, C.G. and Khattab, G. *J Polym Sci, Polym Chem Ed,* 1969, **1,** 217
9 Rooney, J.J. and Stewart, A. in 'Catalysis' (Specialist Periodical Reports) Vol 1, ed. C. Kemball, The Chemical Society, London, 277-334 (1977)