192. *Molecular Size and Shape of Cyclopentadiene Polymers Prepared by Stannic Chloride Catalysis.*

By P. V. French and Albert Wassermann.

Cyclopentadiene can be converted, catalytically by stannic chloride, into polymers, whose molecular weight, M_w, is about 10^4, if oxygen is excluded. On exposure to air the materials absorb oxygen, as shown by analysis and infrared spectrum, and M_w increases up to 10^7, while the intrinsic viscosity is hardly affected. These observations indicate that the polymers contain branched and " looped " chains produced by inter- and intra-molecular oxygen cross-links. The latter are probably responsible for the fact that the critical gel point is not exceeded and that the polymers remain soluble. Some of the results were established with the help of a technique enabling one to determine the light scattering of a dust-free solution in absence of air.

It has been shown [1] that a colourless cyclopentadiene polymer, prepared under catalysis by stannic chloride,[2,3] can be converted into a deeply coloured modification of rather unusual properties. Before elucidating the mechanism of this macromolecular transformation, it is necessary to know the molecular size and shape of the starting material. For this reason we have investigated the light-scattering and viscosity of solutions containing the colourless cyclopentadiene polymer, prepared in absence and in presence of air and characterized by analysis and infrared spectra. Information is here given, for the first time, about the molecular size and shape of a product obtained from cyclopentadiene and a Friedel–Crafts catalyst, notwithstanding many publications * dealing with such polymers.

Experimental

All materials, including the antioxidant α-tocopherol, were commercial samples, except bromobicyclopentyl and " cyclopentamethylenefulvene " (cyclopentadienylidenecyclopentane),

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* See citations on pages 8—12 of ref. 3.

[1] French, Roubinek, and Wassermann, *J.*, 1961, 3974.

[2] Staudinger and Bruson, *Annalen*, 1926, **447**, 97.

[3] French, Ph.D. Thesis, London, 1958.

which were made according to directions of von Braun *et al.*[4] and Kohler *et al.*[5] Cyclopentadiene, stannic chloride, benzene, and chloroform were dried with magnesium perchlorate, metallic calcium, metallic sodium, and calcium chloride, respectively. All reagents and solvents were redistilled, with exclusion of moisture, and their purities were checked by boiling-point and refractive-index measurements. No attempt was made to remove traces of substances which might act as co-catalysts with stannic chloride or as oxidation catalysts during exposure of the polymers to air.

Two classes of cyclopentadiene polymers, α and β, are described, which were made in, respectively, absence and presence of air. In preparing materials α we used an apparatus previously described.[1]

Viscosities were measured with standard U-tube viscometers, the rate of shear being between 200 and 1000 sec.$^{-1}$. The rate of shear had no influence. The measurements of refractive index increments and light-scattering were carried out in apparatus previously described.[1,6] Some interferometric tests were made at a partial pressure of oxygen below 10^{-3} mm. in a special optical cell. Methods of optical clarification and inspection of solutions used for light-scattering have been described.[1,6] There was no fluorescence. If the molecular weight of the polymers was higher than 10^4, dissymetry measurements had to be carried out, which were corrected as prescribed by Sheffer and Hyde.[7] Particle scattering factors were calculated [8] on the assumption that the solute is either a sphere or a random coil; the two sets of computations led to molecular weights agreeing within the specified experimental errors (see Table 4). Cabannes correction factors were determined, but proved insignificant. Light-scattering tests in absence of air were carried out with the cell (a) shown in Fig 1, which was connected with the sintered-glass filter (b) (porosity no. 5) and could be joined, through adaptors and joint (c), to a vacuum-line (see refs. 1 and 3). The air-free solution could be introduced into the evacuated apparatus, which had been freed from dust; slow filtration occurred if the temperature in (a) was slightly lower than that in (b). The cell, together with the filter and the vacuum tap was introduced into the light-scattering apparatus, the cover of which had been replaced by a tight-fitting box of sufficient height. In absence of air the turbidities of solutions containing the cyclopentadiene polymers remained constant for many days, but if air was admitted the turbidities increased continuously until the gel point was reached, the rate of increase being larger for carbon tetrachloride than for benzene solutions. If standard light-scattering cells and solutions saturated with air were used, sufficiently accurate measurements could be made only if α-tocopherol (10^{-4}—10^{-5}M) was added. (Other antioxidants were not tested.) For comparison with some of the light-scattering molecular weights a few isopiestic molecular-weight determinations were carried out at 25·0° in carefully degassed benzene solution (partial pressure of air $<10^{-3}$ mm.), with polymer A of ref. 1 as comparison material.

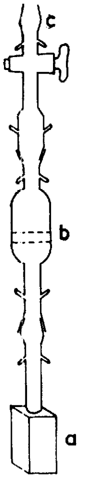

FIG. 1.

Electronic and infrared spectra were measured by Unicam, Perkin-Elmer, and Grubb-Parsons instruments. The infrared spectra of polymer films, of polymer–potassium bromide tablets, and of solutions in carbon disulphide and chloroform were determined; most peak positions agreed within ±0·02 μ. The cyclopentyl derivatives (Table 3) were tested as pure liquids.

RESULTS

Preparation and Analysis.—Initial concentrations of cyclopentadiene and stannic chloride, reaction times, and temperatures are specified in Table 4. Before isolation of the polymers, the stannic chloride was removed as follows. Degassed ammonia or pyridine (0·3 mole/l.) was added to the reaction mixture, and the insoluble adduct thereby formed was filtered or centrifuged off. Monomer consumption, determined by vapour-pressure measurements,[9] was in most tests over 80%. In preparing polymers of class (α), the partial pressure of air was below 10^{-3} mm.; degassed cyclopentadiene was distilled into a degassed solution of stannic chloride in chloroform and, after the polymer had been formed, degassed ammonia was added, filtration being carried

[4] von Braun, Kamp, and Kopp, *Ber.*, 1937, **70**, 1756.
[5] Kohler and Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917.
[6] Buchner, Cooper, and Wassermann, *J.*, 1961, 3974.
[7] Sheffer and Hyde, *Canad. J. Chem.*, 1952, **30**, 817.
[8] Beattie and Booth, *J. Polymer Sci.*, 1960, **44**, 81.
[9] Blakely and Wassermann, *J.*, 1961, 1946.

out without admission of air. The filtrate was freed *in vacuo* from unchanged monomer, ammonia, and chloroform, and the air-free polymer was weighed in absence of air and dissolved in a known weight of degassed solvent. Specific gravities of the resulting solutions were determined in separate experiments after admission of air. The air-free solution of the polymer could be filtered and introduced into the evacuated light-scattering cell shown in Fig. 1. For analysis of the polymer, the solvent was removed *in vacuo* and the residue was introduced into glass vessels which were sealed off *in vacuo* and opened shortly before use.

Polymers of class (β) were prepared in the presence of air by adding stannic chloride containing water (10^{-3} mole/l.), drop by drop, to the cooled solution of cyclopentadiene in chloroform, which was 10^{-2}M with respect to α-tocopherol. After removal of stannic chloride, as described, the solution was added to an excess of ethanol, thereby precipitating the polymer. After repeated dissolution and precipitation, the product was centrifuged and dried *in vacuo* at 20°. The added water may increase the rate of polymerisation and decrease the M_w values (cf. Table 4, lines 1 and 2 of first section and lines 1 and 3 of last section).

TABLE 1.

Analytical composition (%) of cyclopentadiene polymers.

C	H	Cl	Ash *	O †	C	H	Cl	Ash *	O †
		α-Polymers					β-Polymers		
87·7	9·17	3·59	0·00	0·0	88·7	8·26	2·15	0·62	1·3
89·5	8·93	1·43	0·50	−0·3	87·5	8·74	2·02	0·64	1·1
89·0	8·93	1·46	0·40	0·2	86·6	8·77	2·08	0·60	1·9
					88·3	8·83	1·83	0·00	1·0
					86·9	8·73	1·82	0·00	2·5
					87·8	8·92	1·80	0·00	1·5
					86·8	8·11	2·07	0·30	2·1

* The ash contains over 90% of SnO_2; no metal except tin could be detected. † By difference; estimated error ±0·9%.

Table 1 shows representative analytical results. Some polymers were exposed to dry air in the dark at 20° for up to 6 months; insoluble gels were finally formed, of approximate composition $(C_5H_6O_2)_x$, in agreement with earlier observations.[2]

The unsaturation of the polymers was determined by the bromination technique described previously [1,10] (see also ref. 2) and by catalytic hydrogenation. Both sets of experiments showed that 66·0 g. of polymer contained 1·0 ± 0·1 double bond. The correct hydrogen uptake was observed if air was excluded during preparation of the polymer and during hydrogenation. In a typical test 0·704 g. of polymer in 10 ml. of cyclohexane with 0·303 g. of platinum oxide was shaken with hydrogen at 22°/754 mm. for 92 hr.; 0·0202 g. of hydrogen (corrected for uptake by catalyst) was consumed.

Electronic and Infrared Spectra.—In measuring the former, a typical experiment was as follows: a 0·762% solution in chloroform of a polymer, class (β), exposed to air for less than 1 hr., showed optical densities (0·0940 cm. optical path) which increased continuously from 0·01 (400 mμ) to 1·30 (235 mμ). There was neither a peak nor a shoulder, so that there is no evidence for conjugated double bonds, in contrast to the situation with cyclopentadiene polymers made under catalysis by trichloroacetic acid.[1]

Infrared spectra were measured from 2 to 15 μ, the peaks being listed in Table 2. The infrared spectra of the following cyclopentyl derivatives are of interest for comparison: cyclopentane (I), cyclopentanol (II), cyclopentanone (III), bromocyclopentane (IV), cyclopentene (V), cyclopentadiene (VI), bromobicyclopentyl (VII), "cyclopentamethylenefulvene" (cyclopentadienylidenecyclopentane) (VIII), 2- (IX) and 3-cyclopentylcyclopentanol (X), 2-cyclopentylcyclopentanone (XI), 3-cyclopentylcyclopentanone (XII), cyclopentylcyclopentene (XIII), bicyclopentyl (XIV), 3-(cyclopenta-2,4-dienyl)cyclopentanol (XV) and its trichloroacetate (XVI). Peak positions of these materials are given in Table 3 (I—VIII) and in Table 1 of an earlier paper [10] (IX—XVI). Table 2 shows, in the third column, under the heading "reference substance," the cyclopentyl derivatives whose spectra are characterised by a counterpart to the peak in the same line of column 2. The Δμ values in the last column are the maximum discrepancies in μ. The Table shows that there is a general similarity between the infrared

[10] Blakely, Gillespie, Roubinek, Wassermann, and White, *J.*, 1961, 1939.

TABLE 2.

Infrared spectrum of cyclopentadiene polymer. Comparison with the spectra of cyclopentyl derivatives.

(For significance of figures in columns 3 and 4 see text.)

No.	Peak of polymer (μ)	Reference substance*	Δμ
1	2·82m	III, XI, XII	0·08
2	3·00m	II, IX, X, XV	0·06
3	3·25s	V, VI, VIII, XIII, XIV, XV	0·09
4	3·40s	I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI	0·09
5	3·58w	II, IV, V, VII, VIII, IX, XI, XII, XIII, XIV, XV, XVI	0·10
6	3·65w		—
7	3·82w		—
8	3·89w		—
9	4·10w		—
10	5·00w		—
11	5·21w		—
12	5·38w		—
13	5·85w	III, XI, XII, XVI	0·14
14	6·10w	V, VI, VIII, XIII, XV, XVI	0·20
15	6·49w		—
16	6·67w		—
17	6·90s	I, II, III, IV, V, VII, VIII, IX, X, XI, XII, XIII, XIV, XV	0·04
18	7·25sh	I, VI, VIII, XI, XII, XIV	0·10
19	7·40sh	I, II, V, VIII, XI, XII, XIII, XIV, XV, XVI	0·12
20	7·87s	III, IV, V, VI, VII, VIII, X, XI, XII, XIII, XV	0·14
21	8·55m	II, III, V, VII, VIII, IX, X, XI, XIV, XV	0·15
22	8·85m	IV, VII, IX, XI, XIII, XV	0·15
23	9·17m	VI, VIII, X, XI, XII, XIII, XV	0·17
24	9·62m	II, V, VIII, XIV, XV	0·10
25	10·61s	II, VIII, X, XI, XII, XIII, XV	0·09
26	10·94w	III, VI, IX, XI, XIII, XV, XVI	0·06
27	11·40m	IX, XII, XVI	0·10
28	11·87w	VII, X, XVI	0·13
29	12·80m	IX	0·00
30	13·25s	XII	0·00
31	14·20s		—
32	14·75m	VIII, XVI	0·05

spectra of the polymer and of materials containing 5-carbon rings. This is to be expected if one assumes, on earlier chemical evidence,[2] that the repeating unit of the polymer is also a 5-carbon ring rather than a bridged six-membered ring (S) (as in polymers prepared by heating

TABLE 3.

Infrared spectra (μ) of cyclopentyl derivatives I—VIII (see text) (s = <50% transmission).

I	II	III		IV	V		VI		VII		VIII	
3·39s	3·00s	2·79	7·80	3·37s	2·62	7·40	2·58	6·18	3·39s	8·70	3·22	7·85
3·49s	3·38s	2·90	7·90	3·48s	2·67	7·70	2·71	6·30	3·50s	8·80	3·25	7·95
6·90	3·50s	3·36s	8·13	3·51	3·26s	7·80	3·21s	7·32s	6·91s	10·28	3·27	8·15
7·25	6·88	3·46s	8·50	6·25s	3·38s	8·30	3·25s	7·78	7·55	10·80	3·37s	8·55
7·35	6·93	5·72s	8·68s	6·90	3·42	9·60s	3·28s	8·10	7·68	11·15	3·41	9·10
7·60s	7·45s	6·20	9·80	7·00	3·45	9·77	3·46s	9·20	7·78	11·53	3·50	9·22
11·20	7·65	6·80	10·43	7·60	3·50s	10·37	3·70	9·86	7·95	11·82	3·90	9·60
	8·50	6·88	10·98	7·80	6·30	10·10	4·57	10·43	8·05	12·18	6·00s	9·94
	9·30s	7·10s	12·00	8·21s	6·80	14·50	5·43	10·93	8·20	13·60	6·15	10·25
	9·65	7·60	12·35	8·85	6·90		5·53	11·29	8·40	14·60	6·80	10·55
	10·05s			9·75							7·00	11·10
	10·78			10·70							7·30s	11·60s
	11·20			11·10							7·45	12·30
	11·95										7·60	13·10s
											7·70	14·7
												15·95s

cyclopentadiene without a catalyst [11]) or an isoprene residue (I·) (which might be formed by ring opening and hydrogen shift *). Some of the comparisons indicated in Table 2, together with earlier work summarised by Bellamy [12] enable one to assign 12 peaks of the spectrum of the polymer, namely: nos. 1, 2, O–H st; 3, 4, 5, C–H st; 13, C=O st; 14, C=C st; 17, 20, 25, 26, C–H d; and 31, C–Cl st. (st = stretching; d = deformation.)

Refractive-index Increments (Δn), *Molecular Weights, and Viscosities*.—The Δn-values of the polymers (21°, 546 mμ) in carbon tetrachloride and benzene are $0{\cdot}125 \pm 0{\cdot}003$ and $0{\cdot}0394 \pm 0{\cdot}0007$ ml. g.$^{-1}$, respectively, there being no detectable difference between polymers belonging to classes α and β; polymers of the latter class were tested after exposure to air for ½—24 hr. The concentration range of these tests was 0·0665—0·5789 g./dl. For light-scattering and viscosity measurements the concentration range was 0·0600—12·8 g./dl.; in each run at least four concentrations were tested and, as smooth curves were obtained, there was no difficulty in the required extrapolation (see ref. 3).

The molecular weight of one of the polymers (similar to that designated by c in Table 4) was determined isopiestically. The number-average molecular weight obtained was about 20% lower than the light-scattering molecular weight of the same specimen.

The influence of air on the molecular weights, M_w, of these cyclopentadiene polymers is shown in Table 4. Sections (A) and (B) of this Table indicate the mode of preparation and treatment, respectively, of the polymer, before the light-scattering tests were carried out from which M_w and the interaction constants, B, listed in section (C) were derived. The interaction constants are defined by

$$2B = [\partial(Kc/R_\theta/\partial c]_{c\,=\,\mathrm{small}}$$

where K is the "light-scattering constant," c is the polymer concentration, and R_θ is the Rayleigh ratio. The intrinsic viscosities, $[\eta]$, in Table 4 were determined shortly after the light-scattering tests. The solvents used for dilution were 10^{-4}M with respect to α-tocopherol. After the viscosity measurements, the light-scattering of these solutions was re-determined and it was found that the increase of the molecular weight was <20%. The results in Table 4 are typical: eight similar experiments were carried out and the observed increases of the molecular weight, on exposure to air, were all of the same order of magnitude.

TABLE 4.

Results of experiments showing the influence of air on the molecular weight of cyclopentadiene polymers.

(A) *Preparation of polymers.*

Polymer of class	Initial concn. (mole/l.) in C_5H_6	Initial concn. (mole/l.) in $SnCl_4$	Reaction time (hr.)	Temp.	Product dissolved in	Dissolved or solid product divided into portions
α	1·64	0·089	24	20°	C_6H_6	(a) and (b)
β	4·70	0·050	0·5	−5	—	(c) and (d)

(B) *Treatment of portions of polymers.*

(a) Air-free solution in C_6H_6 introduced into evacuated light-scattering cell; no air admitted during test.
(b) Solution in C_6H_6, 2·20 g. of polymer per dl. exposed to dry air at 20° for 66 hr.
(c) Dry powdered polymer dissolved in CCl_4, 10^{-5}M in α-tocopherol; time of exposure of polymer to air <1 hr.
(d) Dry powdered polymer exposed to dry air at 20° for 24 hr.; specimen then dissolved in CCl_4 and tests carried out.

(C) *Results of tests.*

Portion; solvent	M_w (25—27°)	10^5B (mole cm.^{3} g.$^{-2}$)	$[\eta]^{25}$ (dl./g.)
a C_6H_6	$(8{\cdot}8 \pm 2{\cdot}0) \times 10^4$	80 ± 10	$0{\cdot}08 \pm 0{\cdot}01$
b ,, ...	$(1{\cdot}2 \pm 0{\cdot}5) \times 10^6$	$0{\cdot}5 \pm 0{\cdot}2$	$0{\cdot}10 \pm 0{\cdot}01$
c CCl_4	$(7 \pm 2) \times 10^3$	100 ± 20	$0{\cdot}13 \pm 0{\cdot}02$
d ,, ...	$(1{\cdot}0 \pm 0{\cdot}3) \times 10^7$	$0{\cdot}1 \pm 0{\cdot}05$	—

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* The observed unsaturation of the polymer is not compatible with units (S) or (I·) unless one makes the improbable assumption that equal numbers of (S) and (I·) units are present.

[11] Cf. Alder and Stein, *Z. angew. Chem.*, 1934, **47**, 837.

[12] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958.

Fig. 2 shows results for polymers which had been exposed to air for periods from 0·5 to 24 hours (conditions during exposure were as specified in Table 4). The results are best represented by line I, of slope 0·07. If the scale of the ordinate is increased one finds that four of the five points lie on a straight line of a slope 0·12, which is the maximum compatible with these measurements.

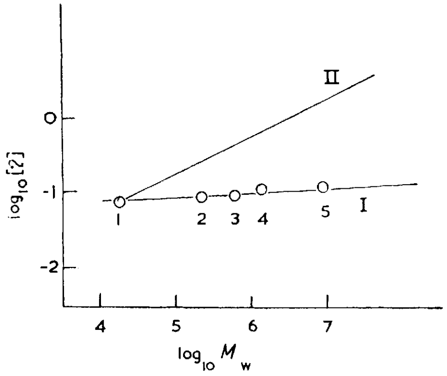

FIG. 2. Plot of $\log_{10} M_w$ (at 25—27°) against intrinsic viscosity $[\eta]$ (where η is in dl./g. at 25°) for polymers of class β in benzene. The points (1)—(5) relate to polymers which had been exposed to dry air at 20° for, respectively, $\frac{1}{2}$, 6, 7, 8, and 24 hr. The experimental observations are represented by line I. For the significance of line II, of slope 0·5, see text.

DISCUSSION

Theoretical considerations[13] have shown that the numerical value of γ in the viscosity–molecular-weight relation

$$[\eta] = \text{Constant} \times M_w^{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is an important indication of the shape of polymers in solution. For linear and stiff particles, γ is larger than 1 (see, for instance, ref. 14); for linear flexible polymers γ is 0·5—1, 0·5 being a lower limit[13] (line II in Fig. 2 represents this limit drawn for comparison). For branched or non-linear polymers,[6,15,16] γ is $<0{\cdot}5$. For spherical solutes[13] $\gamma = 0$. Fig. 2 shows that the γ value of these cyclopentadiene polymers, after exposure to air, is $0{\cdot}07 \pm 0{\cdot}05$, their hydrodynamic behaviour approaching that of spherical " microgels." It is suggested that these species are chain-like macromolecules containing branches and loops, which are formed as indicated below.

The figures in the last column of Table 1 show that polymers which had been exposed to air contain oxygen. It is assumed that not only hydroxyl and carbonyl groups are formed (see p. 1048) but also carbon–oxygen–carbon cross links. This is not incompatible with the infrared spectrum, because C–O–O–C or C–O–C groups cannot always be identified.[12] The suggested cross-linking occurred in the solid polymers or in fairly concentrated solution when the macromolecules were close enough to permit formation of intermolecular oxygen bonds, which are taken to be responsible for the observed increase of molecular weight. The macromolecules can be joined together by terminal carbon atoms, but other junction points are statistically more probable so that branched chains will be produced. Further, thermal movement can bring carbon atoms of one and the same chain so close together that an oxygen bridge can be formed within one chain and thus prevents it from returning to its original more extended configuration. The relative compression of the effective hydrodynamic volume occupied by the macromolecule will increase with chain length, because of increased statistical probability for larger

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[13] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953.

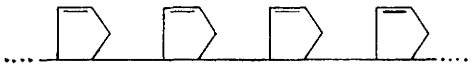
[14] Doty, Bradbury, and Holzer, *J. Amer. Chem. Soc.*, 1956, **78**, 947.

[15] Thurmond and Zimm, *J. Polymer Sci.*, 1952, **8**, 477.

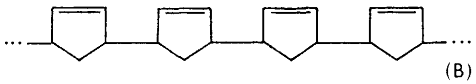
[16] Senti, Hellmann, Ludwig, Babcock, Tobin, Glass, and Lambert, *J. Polymer Sci.*, 1955, **17**, 527.

loops.[17] Intramolecular bonds are probably responsible for the fact that the critical gel point [13] is not exceeded under the specified conditions. The microgels can indeed be converted into insoluble gels (which are probably three-dimensional cross-linked networks) (see p. 1046) but only on prolonged exposure to air.

In order to find out whether formation of loops in these polymers is consistent with stereochemical requirements, four modes of alignments of the repeating units are schematically illustrated. These species contain an isolated double bond per repeating unit and on any one ring the cyclopentene substituents can be *cis*- or *trans*-disposed. The use of accurate space-filling models [18] shows structure (A) to be rather stiff and juxtaposition between carbons of terminal rings can only occur if the degree of polymerization, *P*, is relatively large. In the other structures, both in the all-*cis*- and the all-*trans*-configurations, there is flexibility or the terminal rings are close together even if *P* <10. Thus, there is no stereochemical difficulty in producing the postulated intramolecular oxygen bridges.



(A)



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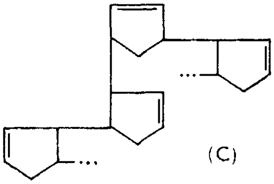

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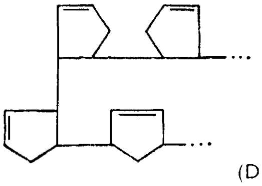

(D)

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[17] Kuhn and Balmer, *J. Polymer Sci.*, 1952, **57**, 311.
[18] Hartley and Robinson, *Trans. Faraday Soc.*, 1952, **48**, 847.