Crystal Structure of Isotactic Poly(*trans*-1,4-penta-1,3-diene)

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ABSTRACT: The crystal structure of isotactic poly(*trans*-1,4-penta-1,3-diene) (—CH$_2$—CH=CH—CH(CH$_3$)—)$_n$ has been determined by X-ray fiber patterns. The unit cell parameters are a = 19.80 ± 0.20, b = 4.86 ± 0.05, c = 4.85 ± 0.05 Å (fiber axis and chain repeat); space group $P2_12_12_1$; $Z = 4$; D_x = 0.97 g/cm^3. The chain conformation in the crystalline state is characterized by a succession of torsional angles of the type skew$^+$, trans, skew$^-$ on the three chain bonds located between double bonds. The side methyl groups are in a cis arrangement with respect to the neighboring trans double bonds. The chain repeat corresponds to one monomer unit, and therefore the asymmetric carbon atoms have the same optical configuration at least for sequences of several units. In the unit cell only isomorphous units are present, so each crystallite must contain isomorphous chain segments.

Stereoregular polymers of 1,3-pentadiene having 1,4 enchainment may belong, in principle, to one of the four types: (a) isotactic, with a cis configuration for the chain double bonds; (b) syndiotactic, with cis double bonds; (c) isotactic, with trans double bonds; or (d) syndiotactic, with trans double bonds. Natta, Porri, and coworkers have succeeded in obtaining all but the last type of polymer,[1–3] and the chain conformations in the crystalline state of the cis polymer have been previously described from X-ray data.[2,3]

As to isotactic, trans polymer I, the observed chain repeat (4.85 ± 0.05 Å) indicates that the conformation of the main chain is similar to that assigned to poly(*trans*-1,4-butadiene) in the modification stable at room temperature[4–6] (Figure 1). This conformation is characterized by an $\bar{S}$TS succession of the internal rotation angles around the single bonds located between successive double bonds, where S (skew) corresponds to about 120° ($\bar{S} = -S = 240°$) and T (trans) to 180°. The side methyl group, however, may occupy either of the two sites indicated in Figure 1, where segments a and b correspond to a skew and to a cis conformation of the $C_3C_2C_1C_5$ sequence, respectively. The smallness of the energy difference between these two conformations was pointed out on theroetical grounds by Mark[7] and later confirmed by Corradini, Frasci, and Martuscelli, who showed that deca-*trans*-7-diene-1,10-dioic acid exists in the crystalline state in two polymorphs, one of which is characterized by a skew, the other by a cis conformation on the single bonds adjacent to double bonds.[8]

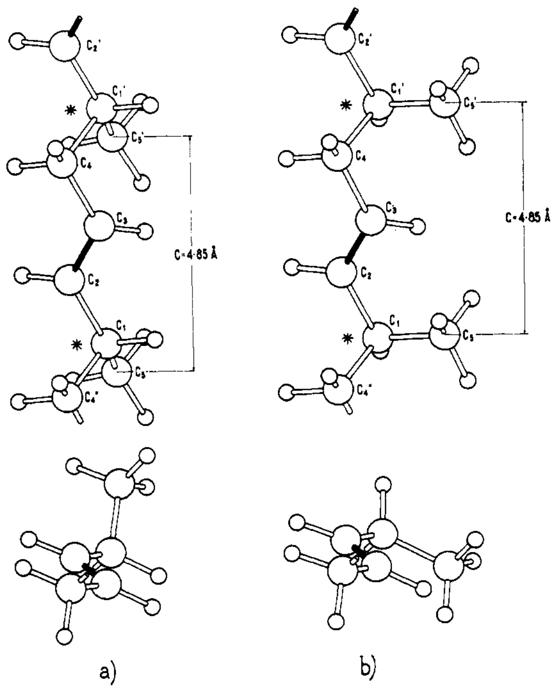

Figure 1. Possible conformations of the macromolecule of isotactic poly(*trans*-1,4-penta-1,3-diene) in the crystalline state. Large circles stand for carbon atoms, small circles for hydrogen atoms. (a) The side methyl groups are in a skew arrangement. (b) The side methyl groups are in a cis arrangement.

TABLE I
GEOMETRIC PARAMETERS ASSUMED FOR THE MACROMOLECULE OF ISOTACTIC POLY(*trans*-1,4-PENTA-1,3-DIENE) IN THE CRYSTALLINE STATE

Dihedral angles, deg			
a		*b*	
$(C_4''C_1C_2)$–$(C_1C_2C_3)$	120	$(C_4''C_1C_2)$–$(C_1C_2C_3)$	120
$(C_1C_2C_3)$–$(C_2C_3C_4)$	180	$(C_1C_2C_3)$–$(C_2C_3C_4)$	180
$(C_2C_3C_4)$–$(C_3C_4C_1')$	240	$(C_2C_3C_4)$–$(C_3C_4C_1')$	240
$(C_3C_4C_1')$–$(C_4C_1'C_2')$	180	$(C_3C_4C_1')$–$(C_4C_1'C_2')$	180
$(C_5C_1C_2)$–$(C_1C_2C_3)$	240	$(C_5C_1C_2)$–$(C_1C_2C_3)$	0
$(C_3C_4C_1')$–$(C_4C_1'C_5')$	60	$(C_3C_4C_1')$–$(C_4C_1'C_5')$	−60
Bond lengths, Å			
C—C 1.54	C=C 1.33	C—H 1.08	
Bond angles			
C—C—C 109° 28′		C=C—C 120°	
H—C—H 109° 28′		C—C—H 109° 28′	

[a] The side methyl group is in the skew arrangement. [b] The side methyl group is in the cis arrangement.

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(7) J. E. Mark, *J. Amer. Chem. Soc.*, **89**, 6829 (1967).

(8) (a) P. Corradini, A. Frasci, and E. Martuscelli, *Chem. Commun.*, 778 (1969). (b) Also, nmr evidence recently obtained by Farina and coworkers indicates that the cis conformation on these bonds is possible in solution for some diene polymers: M. Farina, L. Zetta, and G. Audisio, manuscript in preparation.

TABLE II
COMPARISON BETWEEN THE CALCULATED AND OBSERVED INTENSITIES OF THE X-RAY FIBER PATTERNS OF ISOTACTIC POLY(*trans*-1,4-PENTA-1,3-DIENE) IN THE CRYSTALLINE STATE[a]

hkl	$\left(\frac{\sin\theta}{\lambda}\right)^2 \times 10^4$	I_{calcd}(rel)	I_{obsd}	*hkl*	$\left(\frac{\sin\theta}{\lambda}\right)^2 \times 10^4$	I_{calcd}(rel)	I_{obsd}
200	25	85	mw	501	265	2 } 137	mw
400	102	841	s	311	270	135	
110	113	240	ms	411	315	16	
210	132	2619	s	601	335	68	vw
310	164	398	ms	511	372	104	w
410	209	23	vw	701	418	15 } 28	vw
600	229	195	ms	611	442	13	
510	266	8	vvw	801	514	3	
610	336	3	vvw	711	525	6 } 76	w
800	408	4		021	534	24	
710	419	23 } 204	m	121	541	46	
020	428	78		221	560	128	mw
120	435	103					
220	454	5	vvw	321	592	67	w
320	486	6		811	621	43 } 72	w
810	515	91	w	901	622	5	
420	530	16	vvw	421	636	24	
520	588	41	vw	521	694	42	vw
910	623	11 } 96	mw	911	729	15 } 22	vvw
10.00	637	85		10.01	743	7	
620	658	<1	vvw	621	764	1	
720	741	4 } 7	vvw	721	847	25 } 46	vw
10.10	744	3		10.11	851	21	
820	836	<1		11.01	877	11	
11.10	878	<1		821	942	15 } 27	vvw
12.00	918	<1		11.11	984	12	
920	945	<1		12.01	1024	3	
130	970	2		921	1051	2	
230	989	<1		031	1070	30 } 57	vvw
330	1021	6 } 27	vvw	131	1077	4	
12.10	1025	21		231	1096	23	
430	1066	4 } 10	vvw	331	1128	8	
10.20	1066	6		12.11	1131	1	
530	1123	<1		431	1172	19 } 24	vvw
630	1193	1 } 3	vvw	10.21	1172	5	
13.10	1184	2		13.01	1183	2	
11.20	1200	2		531	1230	11	
14.00	1249	2		631	1300	4 } 12	vvw
730	1276	<1		13.11	1290	2	
12.20	1346	<1		11.21	1306	6	
14.10	1356	<1		14.01	1355	1	
830	1372	<1		731	1383	3	
930	1480	<1		12.21	1453	7 } 15	vvw
13.20	1506	<1		14.11	1463	4	
15.10	1541	<1		831	1478	4	
10.30	1602	<1		15.01	1540	1	
16.00	1632	<1		931	1587	4 } 16	vvw
14.20	1678	2		13.21	1612	12	
040	1714	<1		15.11	1647	3 } 9	vvw
140	1720	<1		10.31	1708	6	
240	1740	<1		16.01	1738	1	
16.10	1739	<1		14.21	1784	1	
11.30	1735	<1					
340	1772	<1		002	425	nF_c^2 = 27	ms^b
440	1816	<1		102	431	nF_c^2 = 219	
540	1874	<1		202	450	nF_c^2 = 83	
12.30	1882	<1		302	482	nF_c^2 = 33	
15.20	1863	<1		402	527	11 } 838	s
				012	532	30	
101	112	185	mw	112	538	47	
201	131	156	m	212	557	103	
301	163	128	m	502	584	267	
401	208	85 } 605	ms	312	589	380	
011	213	259		412	634	34 } 65	w
111	219	261		602	654	31	
211	238	25		512	691	5	

TABLE II (*Continued*)

hkl	$\left(\frac{\sin\theta}{\lambda}\right)^2 \times 10^4$	I_{calcd}(rel)	I_{obsd}
702	737	2	
612	761	46	vw
802	833	1	
712	844	37	
022	853	1 }93	mw
122	860	56	
222	879	1	
322	911	4	
812	940	14 }26	vw
902	941	8	
422	955	28	vw
522	1013	14	
912	1048	33	
10.02	1062	<1	
622	1083	6	
722	1166	3	
10.12	1169	2 }45	vw
11.02	1196	43	
822	1261	3	
11.12	1303	1	
12.02	1343	3	
922	1370	3	
032	1389	1 }9	vvw
132	1395	5	
232	1415	1	
332	1446	5	
12.12	1450	13 }31	vvw
432	1491	1	
10.22	1491	12	
13.02	1502	<1	
532	1548	<1	
632	1619	1	
13.12	1609	47 }61	vvw
11.22	1625	13	
14.02	1674	1	
732	1701	1	
12.22	1771	<1	
14.12	1781	<1	
832	1797	<1	

[a] To account for their multiplicity, the calculated intensities of the (*h*00), (0*k*0), and (00*l*) reflections have been multiplied by 0.5, while those of the (*hkl*) reflections have been multiplied by 2.0. [b] These reflections are clearly visible on tilted fiber patterns.

Therefore, we have been stimulated to undertake a detailed X-ray analysis of I, the results of which are reported here.

Structural Results

Oriented, well-crystallized fibers of I were obtained from stretching a polymer sample under a flow of boiling water. The X-ray fiber pattern is reported in Figure 2. All the reflections are well interpreted assuming an orthorhombic unit cell with $a = 19.80 \pm 0.20$, $b = 4.86 \pm 0.05$, c (chain axis) $= 4.85 \pm 0.05$ Å. The calculated density, with four monomer units per unit cell, is 0.97 g/cm^3, identical with the experimental value.[1] No systematic absences have been observed, with the possible exception of the (*h*00), (0*k*0), and (00*l*) reflections with odd indices. The only space group which contains four general positions in the unit cell and allows a reasonable packing among the chains is $P2_12_12_1$.

Structure factor calculations have been carried out for both models of Figure 1, selecting with trial-and-error criteria the best packing arrangements. The chain models were translated as rigid bodies within the unit cell; the geometric parameters are reported in Table I. Structure factor graphs were employed to miminize the overall disagreement with the observed data. A satisfactory agreement among calculated and observed intensities (Table II) could be obtained only with the model of Figure 1b; the list of atomic fractional coordinates and isotropic thermal parameters for the asymmetric unit is reported in Table III. The resulting packing among the chains is shown in Figure 3, where the shortest C···C intermolecular distances are also indicated; none of them is shorter than 4 Å, in agreement with the usually accepted van der Waals distance between hydrogen-screened carbon atoms.[9]

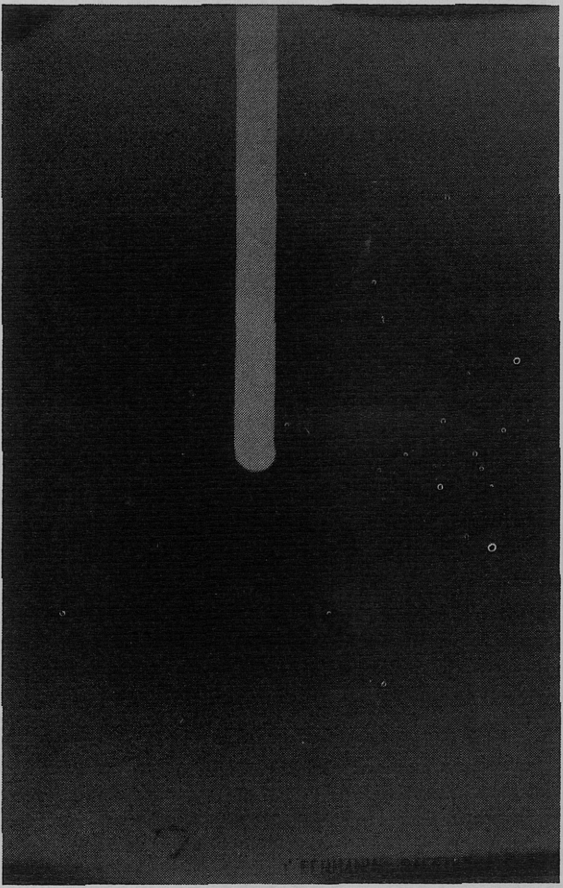

Figure 2. X-Ray fiber photograph of isotactic poly(*trans*-1,4-penta-1,3-diene) in the crystalline state.

It seems interesting to point out that in the $P2_12_12_1$ space group the monomer units contained in the unit cell are all isomorphous among themselves, so that all the tertiary carbon atoms have the same optical configuration. This is also true for isotactic poly(*trans*-1,4-hexa-1,3-diene) (II), which crystallizes with the same space group as I,[10] and for isotactic

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(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 260–261.

(10) G. Perego and I. W. Bassi, *Makromol. Chem.*, **61**, 198 (1963).

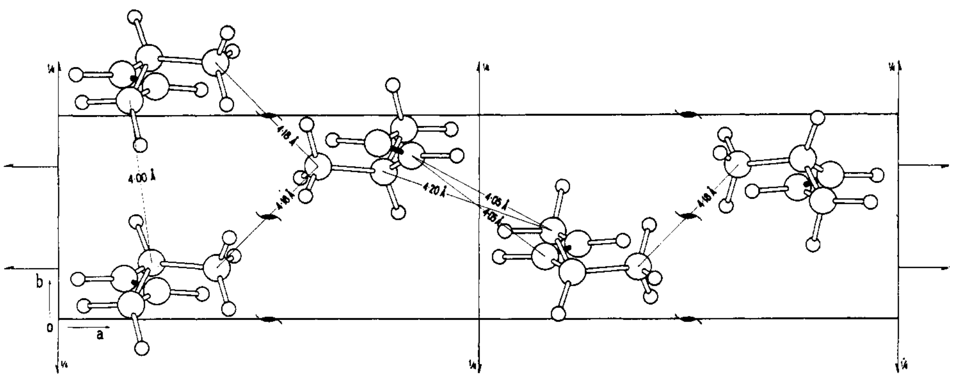

Figure 3. Packing of the macromolecules of isotactic poly(*trans*-1,4-penta-1,3-diene) in the crystalline state.

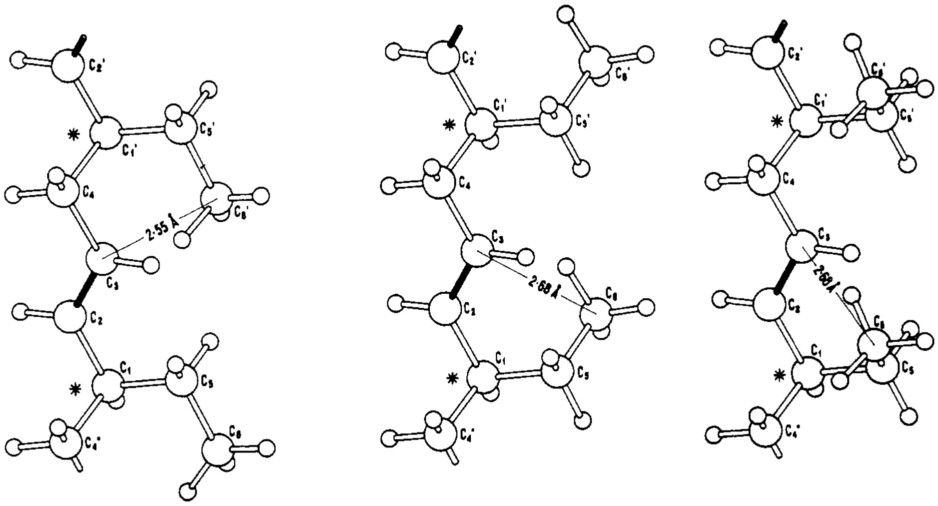

Figure 4. Hypothetical macromolecular configurations of isotactic poly(*trans*-1,4-hexa-1,3-diene). The ethyl side group is in a cis arrangement; the outer methyl group may occupy any of the three positions indicated.

Table III
Atomic Fractional Coordinates of the Asymmetric unit of Isotactic Poly(*trans*-1,4-penta-1,3-diene)

	x/a	y/b	z/c	B, Å^2
C_1	0.11048	0.27263	$\overline{0.12033}$	5.000
C_2	0.07765	0.19805	0.15716	5.000
C_3	0.11679	0.13889	0.38278	5.000
C_4	0.08649	0.06687	0.66027	5.000
C_5	0.18876	0.24794	$\overline{0.10477}$	5.000
H_1	0.09407	0.47325	$\overline{0.17998}$	5.000
H_2	0.02462	0.19547	0.18050	5.000
H_3	0.17109	0.12346	0.35685	5.000
H_4	0.09912	$\overline{0.13632}$	0.71732	5.000
$H_{4'}$	0.03093	0.06687	0.64730	5.000
H_5	0.20265	0.04629	$\overline{0.04772}$	5.000
$H_{5'}$	0.20896	0.30350	$\overline{0.30187}$	5.000
$H_{5''}$	0.20391	0.39609	0.04824	5.000

poly(*trans*-1,4-hepta-1,3-diene) (III), which belongs to the $P2_1$ space group.[11] Therefore, it is reasonable to foresee that for all these polymers a possible optically active sample will show the same crystal structure as observed for the racemic polymers.

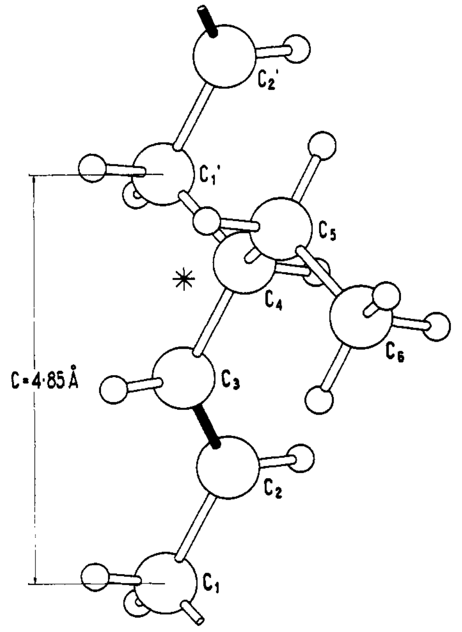

Figure 5. Actual conformation of the macromolecule of isotactic poly(*trans*-1,4-hexa-1,3-diene) in the crystalline state. The side ethyl group is in a skew arrangement.

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(11) G. Natta, I. W. Bassi, and G. Perego, *Atti. Acad. Naz. Lincei*, [8] **34**, 291 (1964).

Conclusions

The macromolecular conformations in the crystalline state of both II and III correspond to the model shown in Figure 1a, provided the methyl group is properly replaced by an ethyl and an *n*-propyl group, respectively. The actual chain structure of II is given in Figure 5. The reason that the side groups of II and III cannot correspond to a cis arrangement of the $C_3C_2C_1C_5$ sequence, as is the case for I (Figure 1b), is readily understood upon examination of the intramolecular nonbonded interactions. In fact, as is shown in Figure 4 with reference to polyhexadiene, any of the three orientations of the methyl group (C_6) obeying the criterion of the staggered bonds gives rise to $C\cdots C$ contact distances much shorter than 3 Å among atoms separated by four bonds and is therefore unacceptable.

As a last remark, let us recall that, of the two C=C—C—C sequences contained in each monomer unit of isotactic poly(*trans*-1,4-penta-1,3-diene) in the crystalline state, one is in the skew, the other in the cis conformation. Since a reasonable conformation of the macromolecule might also be achieved with both sequences in the skew arrangement, our finding is further proof that the cis and the skew conformations have very close energy contents.

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Single Crystal to Single Crystal Transformation of Perhydrotriphenylene Inclusion Compounds during Canal Polymerization of Butadiene

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ABSTRACT: The PHTP–1,3-butadiene inclusion compound (I, $a = 13.35 \pm 0.05$, $b = 14.72 \pm 0.06$, $c = 4.78 \pm 0.02$ Å, $\gamma = 115.3 \pm 0.5°$, space group $P2_1/m$; $Z_{\mathrm{PHTP}} = 2$) undergoes a single crystal–single crystal transformation parallel to the canal polymerization of butadiene to *trans*-1,4-polybutadiene under the action of X or γ rays. The transformation proceeds through an intermediate disordered structure, and has been followed by us by X-ray. The PHTP–polymer inclusion compound (II, $a = b = 14.26 \pm 0.05$, $c = 4.78 \pm 0.02$ Å, $\gamma = 120°$, space group $P6_3/m$, $Z_{\mathrm{PHTP}} = 2$) is virtually identical with PHTP–linear hydrocarbon adducts as far as the host molecules are concerned. While the shape of the channels in II is nearly cylindrical, in I it is markedly elongated, in order to accommodate the included butadiene molecules. During the polymerization the infinite stacks of PHTP molecules undergo a simple rearrangement which does not involve any molecular rotation or packing change within the stacks. The results of the X-ray structural determination are reported for both structures I and II. The terminal C atoms of neighboring butadiene molecules in I are only about 3.50 Å apart, which favors 1,4 addition under the radiation.

Many examples of stereospecific polymerization of irradiated monomers included in the crystalline matrix of the fully equatorial isomer of perhydrotriphenylene (PHTP) have already been reported and discussed from several points of view.[1-4] We recall that all PHPT inclusion compounds are channel-like, in analogy with urea and thiourea complexes.[5] In particular, monomers characterized by different degrees of bulkiness, such as 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, may undergo canal 1,4 trans polymerization in PHTP,[1] while this is possible in urea only for the former,[6] and in thiourea only for the latter monomer.[7] The greater range of possible inclusion compounds obtainable with PHTP is connected with both the size and the shape of the channels being adaptable to the included molecules. This in turn is due to the fact that only weak, nondirectional van der Waals forces are responsible for PHTP molecules being held together in the crystalline state, whereas the crystal structure of urea and thiourea results from a three-dimensional network of intermolecular hydrogen bonds.

A remarkable example which illustrates how molecules with quite a different shape may be accommodated in the channels with a change in crystalline packing is given by the transformation which takes place during the radiation polymerization in PHTP of 1,3-butadiene to poly(*trans*-1,4-butadiene). An interesting feature of this transformation is that it entails a single crystal–single crystal structural change, where the two crystals have different symmetry. We have been able to determine the structure of both crystals as well as to follow the transition, which may occur under the X-ray beam. From the geometry of the channels of the two crystals and from analytical data, significant information has been derived which helps in understanding the mechanism of the polymerization.

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