163. E. Bartel and Z. Grabowski, Roczniki Chem., 31, 27 (1957).
164. L. Filar and S. Winstein, Tetrahedron Letters, 6 (1960).
165. C. Cook and B. Norcross, J. Amer. Chem. Soc., 78, 3797 (1956).
166. C. Cook and B. Norcross, J. Amer. Chem. Soc., 81, 1176 (1959).
167. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 293 (1964).
168. K. Ley, Angew. Chem., 70, 74 (1958).
169. E. Müller, A. Hubell, H. Suhr, and U. Heilmann, Ber., 95, 638 (1962).
170. L. Cohen, J. Org. Chem., 22, 1333 (1957).
171. E. Müller, R. Mayer, U. Heilmann, and K. Scheffler, Annalen, 645, 66 (1961).
172. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 176 (1964).
173. N. A. Vysotskaya, Dokl. Akad. Nauk SSSR, 143, 847 (1962).
174. L. A. Kazitsina, B. S. Kikot', B. V. Rassadin, and O. A. Reutov, Zhur. Obshch. Khim., 33, 223 (1963).
175. V. V. Ershov and G. A. Nikiforov, Dokl. Akad. Nauk SSSR, 158, 1362 (1964).
176. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1335 (1964).
177. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3397 (1963).
178. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3402 (1963).
179. A. Hantzsch, Ber., 40, 330 (1907).
180. A. Hantzsch and K. Meisenburg, Ber., 43, 95 (1910).
181. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3397 (1963).
182. A. Hantzsch and U. Gorki, Ber., 39, 1073 (1906).
183. T. Coffield, A. Filbey, G. Ecke, and A. Kolka, J. Amer. Chem. Soc., 79, 5019 (1957).
184. G. A. Nikiforov and K. M. Dyumaev, Izv. Akad. Nauk SSSR, Ser. Khim., 1068 (1964).
185. A. Balaban, M. Gavat, M. Mocanu, and C. Nenitzescu, Rev. Roumaine Chim., 9, 79 (1964).
186. L. Cohen and W. Jones, J. Amer. Chem. Soc., 82, 1907 (1960).
187. L. Cohen and W. Jones, J. Amer. Chem. Soc., 84, 1625 (1962).
188. L. Cohen and W. Jones, J. Amer. Chem. Soc., 84, 1629 (1962).

Institute of Chemical Physics,
Academy of Sciences of the
USSR, Moscow

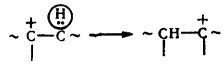
U. D. C. 547.313 : 542.952.6

ANOMALOUS POLYMERISATION OF SOME VINYL MONOMERS

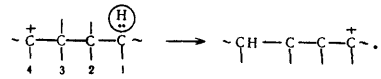
N. D. Prishchepa, Yu. Ya. Gol'dfarb, and B. A. Krentsel'

The problem of the regulation of the chain structure of polymers has always attracted the attention of many investigators. The discovery of stereospecific polymerisation was a great step forward in this direction. One of the interesting possibilities of regulating the chemical structure of macromolecules consists in changing the structure of the monomeric unit during the course of the polymerisation. This process, usually termed conversion or isomerisation polymerisation, results in the growth of the polymeric chain with simultaneous migration of a labile hydrogen atom or group of atoms.

Until now the most characteristic examples of anomalous polymerisation were observed mainly in cationic polymerisations, which are accompanied by the migration of a hydride ion [1]:



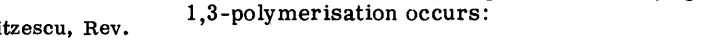
The hydride ion can migrate not only to neighbouring carbon atoms but also to those more distant:



Some authors [2,3] think that the transfer of hydrogen should be sequential: 1–2, 2–3, 3–4, etc.; others [4-6], that the migration takes place directly: 1–3, 1–4, etc.

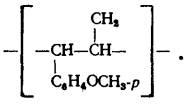
It is noteworthy that hydride transfer reactions have long been known in organic chemistry. Thus, to explain isomerisation, alkylation, cracking, and other reactions, many schemes involving intramolecular or intermolecular migration of hydrogen have been proposed [7-16].

The first suggestions about the possibility of hydrogen migration in polymerisation were made by Staudinger and Dreher [17] in 1935 in studying the polymerisation of β-methylstyrene and acetone. They performed the polymerisation in the presence of tin(IV) chloride and boron trifluoride in toluene at temperatures from 0° to -78° and suggested that polymerisation does not proceed in the usual way but with migration of a labile hydrogen of the methyl group, that is, 1,3-polymerisation occurs:



Ozonation and pyrolysis were used to determine the structure of the polymers. Ozonation did not give results. β-Methylstyrene and acetone, and a little 1,4-diphenylbutadiene and 1,4-di-(*p*-methoxyphenyl)butadiene were detected in the products from pyrolysis at 300°.

The presence of these compounds in the pyrolysis products is attributed to the initial macromolecules having contained structures formed as a result of anomalous polymerisation. Later, a group of Hungarian scientists verified Staudinger and Dreher's results [18]. They polymerised anethole in benzene solution in the presence of tin(IV) chloride and titanium(IV) chloride at room temperature. On investigating the product, they concluded that the polyanethole had the general structure:



On comparing the results of the work of Staudinger and the Hungarian scientists, it is obvious that the conditions of the experiments were not identical; Staudinger carried out the polymerisation at low catalyst concentrations; the Hungarians studied the polymerisation at room temperature with high catalyst concentrations.

Italian scientists investigated the polymerisation of anethole in the presence of aluminium chloride, titanium(IV)

TABLE 1. Polymerisation of anethole on boron trifluoride.

Temperature, °C	Solvent	Degree of polymerisation	No. of C—CH_3 groups present in one molecule	Proportion of 1,2-structure in polymer, %
+15	ether	5.6	3.2	57
+15	ether	5.9	3.7	63
+15	dioxan	4.4	2.7	64
0	ether	7.1	5.5	77
−15	ether	8.3	6.9	83
−77	ether	9.4	7.6	81
−77	petroleum ether	11.2	9.8	87

chloride, and boron trifluoride at various temperatures [19,20]. By using the molecular weight of the polymers and the chemically determined number of CH_3–C groups in the molecule [20], the authors showed the presence of a 1,3-structure in polyanethole. Table 1 shows that a rise in temperature favours 1,3-polymerisation (correspondingly, the proportion of 1,2-structure in the chain decreases).

Kennedy [21] repeated the experiments on the polymerisation of β-methylstyrene and concluded, from the infrared spectra of the polymer obtained in methyl chloride in the presence of aluminium chloride at -60°, that it has the ordinary structure:

$$-\left[\begin{array}{c} CH_3 \\ | \\ -CH-CH- \\ | \\ C_6H_5 \end{array}\right]-.$$

Hence the contradictory results do not allow a definite conclusion to be drawn concerning the nature of the polymerisation of β-methylstyrene and anethole.

In 1955, the attention of our laboratory was drawn to the fact that in poly-(2-methylprop-1-ene) (polyisobutylene) obtained on a Ziegler catalyst the ratio of the number of CH_2 groups differed from the ratio of these groups in ordinary poly-(2-methylprop-1-ene): [22]

$$CH_2=C(CH_3)_2 \rightarrow -CH_2C(CH_3)_2CH_2C(CH_3)_2-, \quad (1)$$

usual structure of poly-(2-methylprop-1-ene)

$$CH_2=C(CH_3)_2 \rightarrow -CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2-. \quad (2)$$

anomalous structure of poly-(2-methylprop-1-ene)

This observation could be interpreted as the polymerisation of 2-methylprop-1-ene on the triethylaluminium + + titanium(IV) chloride catalytic system yielding an anomalous polymer due to hydrogen migration. Because of this a detailed study of the polymerisation of 2-methylprop-1--ene was undertaken. The task was to find conditions under which the migration rate of the labile hydrogen atom would be commensurate with the rate of the ordinary vinyl polymerisation.

Infrared spectroscopy and an analysis of molecular weight distribution were used to determine the structure of the poly-(2-methylprop-1-ene). [23]

The usual method of studying polymers on the ultracentrifuge — from the development of sedimentation diagrams — seemed inapplicable to the poly-(2-methylprop--1-ene)s synthesised; therefore a method was used which allowed the mean molecular weight of any soluble polymers to be determined directly by analysis of the distributed concentrations in the solid layer of a sedimentation cell during the period before the sedimentation equilibrium was established [24].

The sedimentation measurements were made in a large oil ultracentrifuge at 30 000 rev min^{-1}. The molecular weight distribution curves for specimens of poly-(2-methylprop-1-ene) were constructed by use of the weight average M_w and the z-average M_z molecular weights and some model function [25] (see Fig. 1 and Table 2). The correct choice of model function was confirmed for four specimens by a series of experiments which included the measurement of the molecular weights of the specimens by hydrodynamic properties: sedimentation coefficients, diffusion coefficients, and characteristic viscosity [25]. The distribution function of one of the specimens (1) differed significantly from those of the others. It is noteworthy that this specimen was obtained at an Al/Ti ratio of 5 : 1, that is, when the infrared spectra indicate the formation of anomalous structural fragments in the poly-(2-methylprop-1-ene). The infrared spectra showed that an increase in the number of CH_2 groups increases with increased Al/Ti ratios. This indicates the commencement of parts of a new structure of the poly-(2-methylprop-1-ene), where the CH_3/CH_2 ratio is < 2, Eqn. (2), whereas in the ordinary poly-(2-methylprop-1-ene) it equals 2, (Eqn. (1).

Hence two independent physical methods showed the presence of anomalous structural groupings in specimens of poly-(2-methylprop-1-ene) obtained with an excess of trialkylaluminium in the catalyst.

The formation of such structures was observed at ratios Al/Ti > 3. The polymers obtained at other ratios of the components of the catalytic system have the ordinary structure. This has also been shown by American investigators [26], who did not observe an anomalous structure in

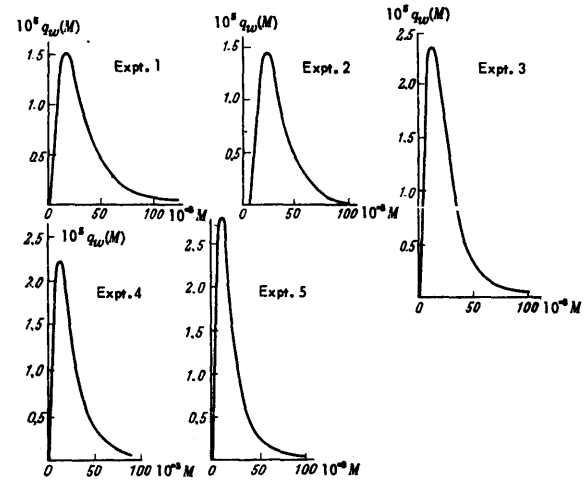


Fig. 1. Molecular weight distribution curves for poly-(2-methylprop-1-ene).

TABLE 2. Functions of the molecular weight distribution of poly--(2-methylprop-1-ene).

Specimen	M_z	M_w	M_n	M_e	$M_{SD_{sm}}$	$M_s[\eta]$	M_z/M_w	β	$10^5 g_w(M_e)$
1	60600	36600	22000	16500	37100	40000	1.66	1.02	2.51
2	42900	38400	26000	22800	21600	24400	1.12	0.71	3.03
3	47300	27200	15000	11600	14100	18500	1.74	1.06	3.55
4	49100	28100	16000	12100	14500	13500	1.74	1.06	3.3
5	38900	23500	14100	10650	6900	3800	1.66	1.02	3.9

the poly-(2-methylprop-1-ene) which they obtained on a Ziegler catalyst at ratios of Al/Ti = 2 or less.

After the publication of a paper on the conversion polymerisation of 2-methylprop-1-ene[22] attention was directed to the possibility of carrying out the 1,3-polymerisation of propene[27]. It was suggested that, depending on the reaction conditions and the catalyst used, the polymerisation can be directed to the formation of a 1,2-structure, Eqn.(3); a 1,3-structure, Eqn.(4); or their mixture, Eqn.(5):

$$CH_2{=}CH(CH_3) + [Cat] \rightarrow \sim CH_2CH(CH_3)\ldots[Cat], \quad (3)$$

$$\sim CH_2{-}\overset{\oplus}{C}H\ldots[Cat] \longleftrightarrow \sim CH{=}CH{-}CH_3\ldots[Cat], \quad (4)$$

$$\sim (CH_2)_nCH(CH_3)\,CH_2\,(CH_2)_nCH(CH_3)\,CH_2\sim. \quad (5)$$

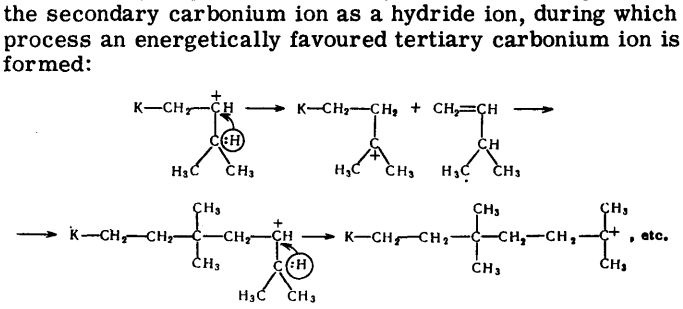
The realisation of such an anomalous polymerisation of propene, as well being of exceptional scientific value, is of great practical interest, since with its aid a single monomer (propene) can yield a series of polyalkenes of different structure and properties. The recently published investigation of the 1,3-polymerisation of propene and study of the properties of the polymer obtained therefore merits attention[28].

The polymerisation was carried out in the presence of the catalytic system VCl_4.Fe(acetylacetonate) + $Al(C_2H_5)_3$. Infrared spectroscopy was used to identify the structure of the polymers. It was found that the degree of migration of hydrogen during polymerisation depends on the solvent. When the polymerisation is carried out in n-heptane, a polymer with the usual 1,2-structure is obtained. In benzene and its derivatives a polymer is obtained with the structure of a copolymer of ethylene and propene. An increase in the pressure and temperature of the reaction brought about an increase in the amount of copolymer. Polyethylene was obtained from propene when the polymerisation was carried out in dichloroethane. The X-ray diagram of the product showed that it has a crystal structure similar to that of polyethylene.

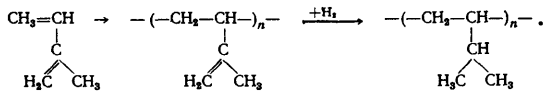
The conversion polymerisation of 3-methylbut-1-ene has been studied most[29,30]. The polymerisation was performed at low temperatures in ethyl chloride solution; aluminium chloride was used as catalyst. The polymer was obtained as colourless crystals, m.p. 55°, with molecular weight ~ 55 000. The infrared and NMR spectra of this polymer differed from those obtained from the polymer produced on a Ziegler catalyst. The authors proposed the following polymerisation mechanism: the cation attacks the molecule of the monomer, forming a secondary carbonium ion:

$$K^+ + CH_2{=}CH \rightarrow K{-}CH_2{-}\overset{+}{C}H$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\quad |$$
$$\qquad\quad CH(CH_3)_2 \qquad\quad CH(CH_3)_2 .$$

The labile hydrogen at the tertiary carbon atom migrates to the secondary carbonium ion as a hydride ion, during which process an energetically favoured tertiary carbonium ion is formed:

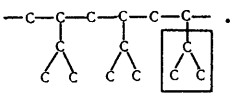


For a more convincing proof of the presence of the anomalous structure in the polymer synthesised on aluminium chloride the normal poly-(3-methylbut-1-ene) was synthesised by directed 1,2-polymerisation of isoprene with subsequent hydrogenation[31]:



The NMR spectrum of this product agreed with that of poly-(3-methylbut-1-ene) obtained on Ziegler catalyst and differed from that of poly-(3-methylbut-1-ene) synthesised on cationic catalysts. The relative proportions of anomalous and ordinary structures were determined by pyrolysis of the polymer with subsequent quantitative analysis of the gaseous products by gas chromatography and investigation of the liquid products of the pyrolysis by infrared spectroscopy. Analysis of the gaseous pyrolysis products of an isotactic polymer obtained on a Ziegler catalyst and of a hydrogenated 3,4-polyisoprene showed concentrations of 65.4 and 66.7 mole % C_3 fragments, which are formed only in the ordinary polymerisation of 3-methylbut-1-ene:

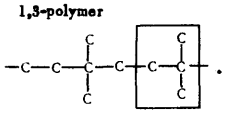
1,2-polymer



C_3 fragments

In the pyrolysis of anomalous poly-(3-methylbut-1-ene), synthesised in the presence of cationic catalysts at -96°, only 20.7 mole % C_3 fragments and 30 mole % 2-methylprop-1-ene C_4 fragments are formed:

1,3-polymer

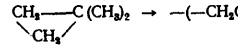


C_4 fragments

The proportions of 2-methylprop-1-ene fraction in the pyrolysis of an isotactic polymer and of hydrogenated polyisoprene are 9.1 and 5.3 mole % respectively. Evidently the ratio of the amounts of C_3 and C_4 fragments depends on the presence in the polymer of ordinary and anomalous structures.

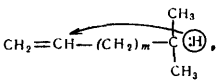
The amount of 1,3-structure in polymers obtained on cationic catalysts at temperatures from -78° to -96° reaches 70%. The infrared spectra of the liquid pyrolysis products of poly-(3-methylbut-1-ene) confirm the gas chromatographic results.

Additional proof of the presence of a 1,3-structure in poly-(3-methylbut-1-ene) is obtained in the polymerisation of 1,1-dimethylcyclopropane on aluminium bromide[32]:



The infrared spectrum of the polymer thus obtained agrees completely with the spectrum of anomalous poly-(3-methylbut-1-ene).

Edwards and Chamberlain investigated the migration of hydride ion in the polymerisation of methylalk-1-enes of the type:



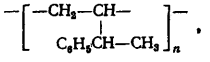
on cationic catalysts[33] and found that for $m = 0$ — for 3-methylbut-1-ene — 1,3-polymerisation proceeds throughout the entire temperature range studied (from 0° to -73°). For $m = 1$, the transfer path of the hydride ion is longer; therefore polymerisation at 0° leads to the production of only an insignificant amount of the 1,4-polymer. However, on lowering the temperature to -73° 1,4-polymerisation predominates.

For $m = 2$ and 0°, 1,5-polymerisation is almost absent; at -73°, <50% of the 1,5-polymer is formed. This shows that at lower temperature the migration of hydride ion is easier than ordinary vinyl polymerisation. Apparently, as the temperature is raised the growth rate increases more rapidly than the hydride ion migration rate, and consequently the growth activation energy is greater than the hydride ion migration activation energy.

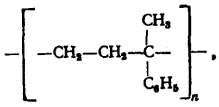
Somewhat in contradiction to Edwards and Chamberlain's results is the work of Goodrich and coworkers[34], in which it was shown that a low temperature is not necessary for the anomalous polymerisation of 4-methylpent-1-ene. These authors carried out the polymerisation in the temperature range from 0° to 60° in n-heptane solution; as catalyst, they used certain derivatives of transition metals and alkylaluminium halides.

The principal results of the workers cited above[29-33] were recently confirmed again[35]. The structure of poly-(3-methylbut-1-ene), poly-(4-methylpent-1-ene), and poly-(6-methylhept-1-ene), obtained in polymerisation on Friedel–Crafts catalysts in ethyl chloride and heptane at temperatures from 0° to -78° was studied. An anomalous structure was present in all these polymers and it was found that the ratio of anomalous structure to ordinary: (1) is independent of the type of catalyst; (2) increases with the dielectric constant of the solvent; (3) increases at lower temperatures.

Mention must also be made of work[36] on the polymerisation of 3-phenylbut-1-ene. When this compound is polymerised in ethyl chloride solution at -78° in the presence of aluminium chloride, in addition to the polymer of expected structure:

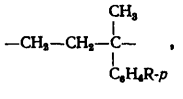


a polymer with the 1,3-structure:



is obtained in 56% yield. The structure of the polymer was determined with the aid of NMR and infrared spectra.

It is interesting that according to the infrared spectrum the polymer contains mono- and di-substituted benzene rings:



where R = H or $CH_3-CH-CH-CH_3$ (with C_6H_5 on the second CH), that is, alkylation of the benzene ring takes place in addition to the anomalous polymerisation. However, during alkylation the isomerisation of the secondary and the (energetically more favourable) tertiary carbonium ions does not take place. The authors explain this by the fact that under certain conditions the rate of alkylation of the benzene ring can be greater than the rate of rearrangement.

From certain other monomers which are apparently capable of polymerisation with migration of a hydride ion, mention may be made of the compounds of type:

$$\text{cyclo-}C_6H_{11}[CH_2]_nCH{=}CH_2 \text{ and cyclo-}C_5H_9[CH_2]_nCH{=}CH_2.$$

These substances have similar structure fragments to compounds of the 3-methylbut-1-ene type and therefore should be capable of anomalous polymerisation. The anomalous polymerisation of these cyclic monomers makes possible the introduction into the polymeric chain of the cyclohexyl or cyclopentyl ring, which should markedly change the properties of the polymer. Ketley and Ehrig[37] studied the polymerisation of such a type of monomer. The infrared spectra of poly(vinylcycloalkanes) and poly(allylcycloalkanes) obtained on Ziegler–Natta catalysts showed that the polymers have the normal structure (Fig. 2).

The absorption bands characteristic of different sequences of methylene groups for the polymers obtained on Friedel–Crafts catalysts are shown in Table 3. The presence of absorption bands characteristic of the groups

$$-(-CH_2-CH_2-)- \text{ and } -(-CH_2-CH_2-CH_2-)-,$$

which belong respectively to poly(vinylcyclohexane) and poly(allylcyclohexane) (Fig. 3), obtained on cationic catalysts and the absence of these bands from the spectra of the polymers obtained on Ziegler–Natta catalysts, shows that in polymerisation on cationic catalysts hydrogen migration

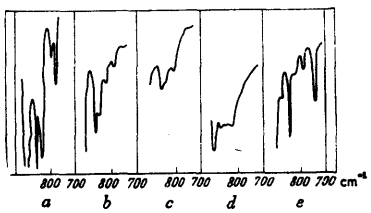


Fig. 2. Infrared spectra of polymers obtained on Ziegler–Natta catalysts:
a) vinylcyclohexane; *b*) allylcyclohexane;
c) vinylcyclopentane; *d*) allylcyclopentane;
e) 5-cyclohexylpent-1-ene.

TABLE 3. Absorption bands of the methylene groups of polycyclohexylalkenes and poly(cyclopentylalkenes) obtained on Friedel–Crafts catalysts.

Polymer	Absorption band, cm⁻¹	Fragment of structure
Poly(vinylcyclohexane)	748	$-(-CH_2-)_3-$
Poly(allylcyclohexane)	725	$-(-CH_2-)_3-$
Poly(vinylcyclopentane)	—	—
Poly(allylcyclopentane)	750	$-(-CH_2-)_2-$
Poly-(5-cyclohexylpent-1-ene)	721	$-(-CH_2-)_5-$

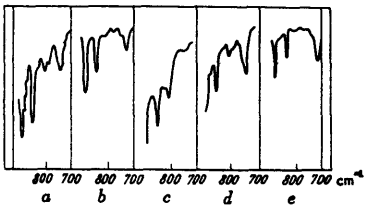
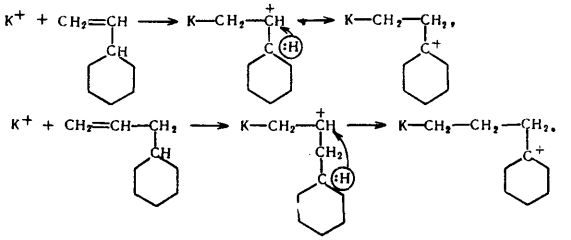


Fig. 3. Infrared spectra of polymers obtained on Friedel–Crafts catalysts:
a) vinylcyclohexane; *b*) allylcyclohexane;
c) vinylcyclopentane; *d*) allylcyclopentane;
e) 5-cyclohexylpent-1-ene.

takes place, leading to the formation of anomalous polymers:



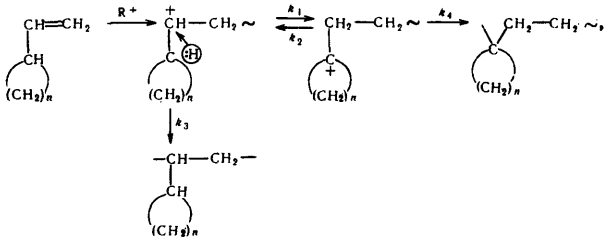
The strong absorption band at 721 cm^{-1} in poly-(5-cyclohexylpent-1-ene) obtained on cationic catalysts supports the structure:

$$-CH_2CH_2CH_2CH_2CH_2C_6H_{10}-.$$

Poly-(5-cyclohexylpent-1-ene) obtained on a Ziegler–Natta type catalyst has an absorption band at 730 cm^{-1}, which corresponds to

$$-(-CH_2-CH_2-CH_2-)-$$

in the lateral cyclohexylpropyl groups. Poly(vinylcyclopentane) obtained on cationic catalysts does not have an absorption band in the range 740–745 cm^{-1}. Hence it can be concluded that this is an ordinary 1,2-polymer. The fact that isomerisation polymerisation takes place with vinylcyclohexane, whereas for vinylcyclopentane there is the usual 1,2-polymerisation, is rather unexpected. The authors propose the following scheme of polymerisation of this type of monomer:



where k_3 should be approximately the same for cyclohexyl and cyclopentyl compounds. It can therefore be assumed that the ion formed initially during the polymerisation of vinylcyclopentane is not isomerised. When it is subjected to isomerisation then the carbonium ion which is formed is less active than in vinylcyclohexane.

The 750 cm^{-1} absorption band in the infrared spectrum of poly(allylcyclopentane) obtained on a Friedel–Crafts catalyst corresponds most likely to the $-(CH_2-CH_2-)$ groups, and not $-(CH_2-CH_2-CH_2)-$. Therefore the anomalous structure of this polymer can be represented as $-CH_2CH_2CH(C_5H_9)-$. The chain growth of poly(allylcyclopentane) will proceed with greater probability with the participation of a secondary carbonium ion situated close to the ring.

Simultaneously with Ketley and Ehrig's work appeared that of Kennedy and coworkers, which was also devoted to an investigation of the anomalous polymerisation of vinylcyclohexane[38]. The polymerisation of vinylcyclohexane was studied from -144° to +7° (catalyst, $AlCl_3$; the solvent, ethyl chloride) and from 60° to 85° (catalyst, $AlEt_3 + TiCl_4$; solvent, n-heptane). From the infrared and NMR spectra, the authors concluded that the 1,3-structure predominates in polymers obtained on aluminium chloride at temperatures below -100°. The melting points of poly(vinylcyclohexane)s containing chains with an anomalous structure were considerably lower (70–120°) than those of polymers with a 1,2-structure (200°).

The results suggest that isomerisation polymerisation of both 3-methylbut-1-ene and vinylcycloalkanes depends on the ability of the corresponding hydrogen atom to migrate, the stability of the tertiary carbonium ion formed, and its activity with respect to the monomer molecules.

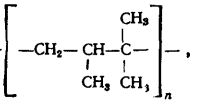
It must be noted that in addition to the communications devoted to polymerisation with hydride ion migration there are some reports of the possibility of migration of other groups or atoms. One of the first of these was made by Meier[39], who advanced the possibility of the migration of a methyl group in the polymerisation of 3,3-dimethylbut-1-ene:



However, he did not produce experimental proof of the proposed scheme.

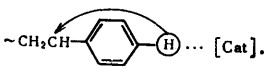
Edwards and Chamberlain suggested that in view of the similarity in the structures of 3-methylbut-1-ene and 3,3-dimethylbut-1-ene, polymerisation by migration of a methyl group (analogous to the hydrogen atom in 3-methylbut-1-ene) could be expected[33]. However, they did not succeed in obtaining a 1,3-polymer in the polymerisation of 3,3-dimethylbut-1-ene in the presence of aluminium chloride at 0°. The authors attributed their failure to steric hindrance.

Kennedy and coworkers repeated this work[40] and suggested that the reason for Edwards and Chamberlain's failure is the high rate of chain breaking after the migration of the methyl group. The authors assumed that the reaction of chain transfer or breaking requires a greater activation energy than isomerisation and growth and therefore the migration of the methyl group will take place more readily at a lower temperature. When the polymerisation of 3,3-dimethylbut-1-ene was carried out in the temperature range from -30° to -130° a trimer of 3,3-dimethylbut-1-ene was obtained. Polymerisation at a lower temperature (-130°) led to the production of an amorphous polymer. On the basis of the infrared and NMR spectra, Kennedy and coworkers proposed the following structure for this polymer:



that is, it can be assumed that in the polymerisation at -130°, migration of the methyl group precedes the growth

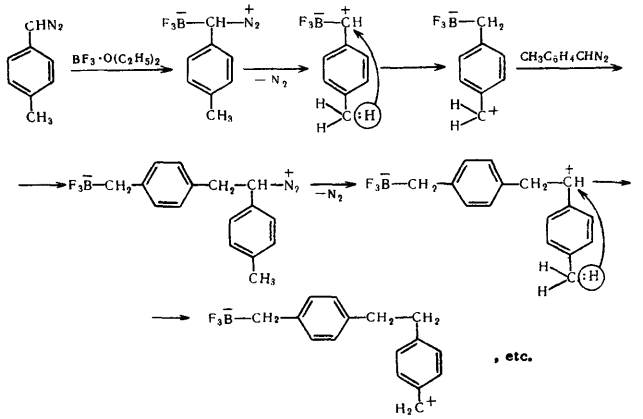
reaction, forming the energetically more favourable tertiary carbonium ion. The possibility of anomalous polymerisation of styrene with inclusion of the benzene ring in the main polymeric chain has been suggested[27]:



The first experimental proof of this hypothesis was obtained in our laboratory[41]. In the polymerisation of styrene on the system $AlEt_3$ + $VOCl_3$ a polymer was obtained from which a small fraction insoluble in benzene, with m.p. 310–315°, could be isolated. An absorption band with maximum 809 cm^{-1} was observed in the infrared spectrum of this polystyrene; it is characteristic for the 1,4-disubstituted benzene ring.

It was suggested that in the polymerisation of styrene transfer of an active centre in the *ortho*- or *para*-position to the vinyl group occurs. During this reaction the benzene or quinonoid structures are included in the main chain of the polymeric molecule. However, later investigations showed that such a possibility is ruled out.

Korshak and coworkers[42] obtained polymers including benzene rings by a somewhat unusual route. They observed that in the decomposition of phenyldiazomethane in the presence of $BF_3.O(C_2H_5)_2$ a polymer containing methylene and phenylene groups in the main chain is formed. The authors explained this fact by the partial isomerisation of phenyldiazomethane during polymerisation. The study of the infrared and NMR spectra of polymers obtained during the decomposition of 4-methylphenyldiazomethane in the presence of $BF_3.O(C_2H_5)_2$ showed the high concentration of methylene groups in the polymer. The conclusion was drawn that in the decomposition of 4-methylphenyldiazomethane formation of a polymer containing methylene and phenylene groups takes place. A mechanism for the polymerisation is proposed in which the transfer of a hydride ion to the cation being formed is realised:



In some instances the realisation of anomalous addition can have practical value. An example of this has already been mentioned — the production of copolymers of ethylene and propene as a result of the conversion polymerisation of propene.

It is possible that a way will be found of carrying out the conversion polymerisation in those instances where the direct synthesis of the polymer from the monomer by ordinary means is impossible, for example, with poly(vinyl alcohol). The conversion polymerisation of acetaldehyde can in principle lead to the direct formation of polyvinyl alcohol:

$$CH_3CHO \rightarrow -CH_2-CH(OH)-.$$

1. J.P.Kennedy and A.W.Langer, Adv.Polymer Sci., 3, 509 (1964).
2. F.C.Whitmore and F.Johnston, J.Amer.Chem.Soc., 55, 5020 (1933).
3. F.C.Whitmore and F.Johnston, J.Amer.Chem.Soc., 60, 2265 (1938).
4. P.S.Skell and I.Starter, J.Amer.Chem.Soc., 84, 3962 (1962).
5. P.S.Skell and R.J.Maxwell, J.Amer.Chem.Soc., 84, 3963 (1962).
6. G.J.Karabatsos and C.E.Orzech, J.Amer.Chem.Soc., 84, 2838 (1962).
7. A.D.Ketley and M.C.Harvey, J.Org.Chem., 26, 4649 (1961).
8. V.N.Ipatieff, H.Pines, and L.Schmerling, J.Org.Chem., 5, 253 (1940).
9. B.S.Friedman and F.L.Morritz, J.Amer.Chem.Soc., 78, 2000 (1956).
10. A.Michael and F.Zeidler, Annalen, 393, 81 (1912).
11. T.H.Zink and K.Zahn, Ber., 43, 849 (1910).
12. V.N.Ipat'ev and V.Leonovich, Zhur.Russ.Fiz.-Khim. Obshch., 35, 606 (1903).
13. H.Pines and J.M.Mavity, in "The Chemistry of Petroleum Hydrocarbons" (Edited by B.T.Brooks, G.E.Boord, S.T.Kurtz, and L.Schmerling), Reinhold, New York, 1955, Vol.3, Chapter 39.
14. B.T.Brooks, *ibid.*, Chapter 44.
15. L.Schmerling, *ibid.*, Chapter 54.
16. N.C.Deno, H.J.Peterson, and G.S.Saines, Chem.Rev., 60, 7 (1960).
17. H.Staudinger and E.Dreher, Annalen, 517, 73 (1935).
18. A.Müller, L.Toldy, and Z.Racz, Ber., 77, 777 (1944).
19. A.Rattu and M.Secci, Rend.Seminiario Fac.Sci.Univ. Cagliari, 26, 118 (1956).
20. M.Secci and L.Mameli, Ann.Chim.(Italy), 47, 580 (1957).
21. J.P.Kennedy, J.Polymer Sci., A2, 5171 (1964).
22. A.V.Topchiev, B.A.Krentsel', N.F.Bogomolova, and Yu.Ya.Gol'dfarb, Dokl.Akad.Nauk SSSR, 111, 121 (1956).
23. Yu.Ya.Gol'dfarb, Candidate's Thesis, Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow, 1964.
24. S.Ya.Frenkel', A.V.Topchiev, B.A.Krentsel', Yu.Ya.Gol'dfarb, and L.M.Pyrkov, Zhur.Fiz.Khim., 33, 2778 (1959) [Russ.J.Phys.Chem., 625 (1959)].
25. S.Ya.Frenkel', A.V.Topchiev, B.A.Krentsel', and Yu.Ya.Gol'dfarb, Zhur.Fiz.Khim., 34, 327 (1960) [Russ.J. Phys.Chem., 153 (1960)].
26. R.Bacskai and S.J.Lapporte, J.Polymer Sci., A1, 2225 (1963).
27. K.Mienes, Kunststoffe–Plastics, 8, 469 (1961).
28. Sadao Yuguchi and Masao Iwamoto, J.Polymer Sci., B2, 1035 (1964).
29. J.P.Kennedy and R.M.Thomas, Makromol.Chem., 53, 28 (1962).
30. J.P.Kennedy and R.M.Thomas, Makromol.Chem., 64, 1 (1963).
31. J.P.Kennedy, L.S.Minckler, G.G.Wanless, and R.M.Thomas, J.Polymer Sci., A2, 1441 (1964).
32. A.D.Ketley, J.Polymer Sci., B1, 313 (1963).
33. W.R.Edwards and N.F.Chamberlain, J.Polymer Sci., A1, 2299 (1963).
34. J.E.Goodrich and R.S.Porter, J.Polymer Sci., B2, 353 (1964).

35. A.D.Ketley, J.Polymer Sci., B2, 827 (1964).
36. J.P.Kennedy, C.A.Cohen, and W.Naegele, J.Polymer Sci., B2, 1159 (1964).
37. A.D.Ketley and R.J.Ehrig, J.Polymer Sci., A2, 4461 (1964).
38. J.P.Kennedy, J.J.Elliott, and W.Naegele, J.Polymer Sci., A2, 5029 (1964).
39. R.L.Meier, J.Chem.Soc., 3656 (1950).
40. J.P.Kennedy, J.J.Elliott, and B.E.Hudson, Makromol. Chem., 79, 109 (1964).
41. B.A.Krentsel', L.G.Sidorova, M.V.Shishkina, M.M.Kusakov, F.V.Korenevskaya, and V.V.Shchekin, Neftekhimiya, 2, 705 (1962).
42. V.V.Korshak, V.A.Sergeev, V.K.Shitikov, and P.Sh.Burenko, Vysokomol.Soed., 5, 1597 (1963).

Institute of Petrochemical Synthesis,
Academy of Sciences of the USSR,
Moscow

U.D.C. 547.29:547.39

β-ELIMINATION IN THE β-SUBSTITUTED PROPIONIC ACID SERIES

P. F. Butskus and G. I. Denis

CONTENTS

1. β-Substituted propionic acids 839
2. Esters of β-substituted propionic acids 840
3. Amides of β-substituted propionic acids 841
4. Nitriles of β-substituted propionic acids 841
5. Alkylations with the aid of β-substituted propionic acids and their derivatives 843
6. Mechanism of β-eliminations 844

It has long been known that β-substituted propionic acids and their derivatives have a tendency to undergo β-elimination:

$$ACH_2CH_2X \rightarrow AH + CH_2{=}CHX$$

where A = halogen, HO, RO, RS, RSO_2, H_2N, RNH, or $(R)_2N$, etc., and X = COOH, COOR, $CONH_2$, or CN.

These reactions are of both theoretical and practical interest. However, up to recently information on this subject had not been summarised. The present review covers factual information on the β-elimination of β-substituted propionic acids, their esters, amides, and nitriles.

1. β-SUBSTITUTED PROPIONIC ACIDS

β-Halogenopropionic acids are converted into acrylic acid by distillation[1]; by heating under pressure[2] or under vacuum[3]; by heating in the presence of activated charcoal[3] or aluminium oxide[4]; by boiling with water[5] or with aqueous solutions of alkalis[5-11]; and by the action of sodium carbonate[11], lead oxide[11-13] or carbonate[12], alkali metal alkoxides[6], sodium acrylate[14], or diethylaniline[9,10]. Several attempts to synthesise β-alanine and its methyl ester from β-bromopropionic acid led to the preparation of acrylic acid[15]. When β-iodopropionic acid is treated with an excess of silver oxide, a polymer of acrylic acid is formed[16-18].

In 1862 Beilstein noted[12] that, when salts of β-hydroxypropionic acid are heated to 200–250°, salts of acrylic and diacrylic acid are formed. Later this reaction was also observed by Wislicenus[13,19]. Acrylic acid is formed when β-hydroxypropionic acid is heated to boiling, or when the acid itself, or its salts, is distilled with sulphuric acid[12,13,19-22]. When β-hydroxypropionic acid is evaporated with hydrochloric acid, a polymer of acrylic acid is formed[16-18]. Acrylic acid is obtained from a mixture of β-hydroxypropionic acid, diacrylic acid, and acrylic acid polymer[23], and also from 2-hydroxypropiononitrile[24-28].

At 190–225°, and in the presence of alkali or alkaline-earth salts of the same acids, β-alkoxypropionic acids (containing C_1 to C_{17} alkoxy-groups) give acrylic acid in good yield[29]. When β-ethoxypropionic acid is heated in the presence of *p*-toluenesulphonic acid and hydroquinone, a mixture of acrylic acid and its ethyl ester is formed[30,31]. According to the patent literature, 2-dicarboxydiethyl ether gives acrylic acid when it is treated in the gas phase at 150–185° with activated charcoal soaked in phosphoric acid[32]. In an alkaline medium, β-carboxyethyl esters of monohydric and dihydric phenols give decarboxyethylation products[33-38]. When heated for a short time to 180–190° in the presence of hydroquinone, β-acetoxypropionic acid decomposes according to the following reaction[39]:

$$CH_3COOCH_2CH_2COOH \rightarrow CH_3COOH + CH_2{=}CHCOOH.$$

The yield of acrylic acid is 77%. The removal of the β-carboxyethyl group in esters of phosphoric acid[40-43] has been studied. Methods of synthesising α- and β-substituted acrylic acids from α- and β-substituted β-hydroxypropionic acids and their esters at the hydroxy-group have been developed[44-59].

When 2-carboxyethyl aryl sulphones are boiled with 10% sodium hydroxide, cleavage occurs according to the following scheme[60]:

$$ArSO_2CH_2CH_2COOH \rightarrow ArSO_2H + CH_2{=}CHCOOH.$$

Mulder[61] observed that β-aminopropionic acid decomposes into acrylic acid and ammonia when it is heated to about the melting point. β-Diethylaminopropionic acid decomposes in the same way (160°):[62]

$$(C_2H_5)_2NCH_2CH_2COOH \rightarrow (C_2H_5)_2NH + CH_2{=}CHCOOH.$$

When heated to its melting point, the betaine of β-trimethylaminopropionic acid gives ammonium acrylate[63]. The decarboxyethylation of *N*-(2-carboxyethyl)-α-amino-acids has been studied[34]. Heating of 2,2'-dicarboxydiethylamine with phthalic anhydride leads to the formation of *N*-(2-carboxyethyl)phthalimide and acrylic acid in quantitative yield[64].

Attempts to cyclise *N*-(2-carboxyethyl)-*N*-acycl-*p*-anisidines to the corresponding quinolones led to decarboxyethylation[65]. When *N*-(2-naphthyl)-β-aminopropionic acid is heated for 2–3 min at 220°, 1-naphthylamine and acrylic acid are formed[66].