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Network Formation of Polyurethanes Due to Side Reactions

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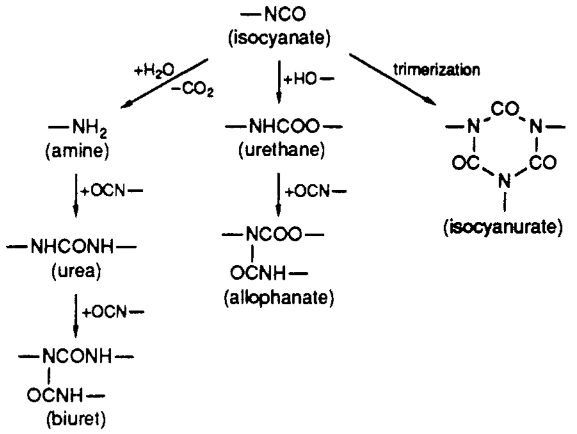
ABSTRACT: A theoretical approach based on the theory of branching processes has been developed to describe gelation and network formation in polyurethane systems as a result of side reactions: formation of allophanate, urea, biuret, and isocyanurate groups. The branched and cross-linked structures are assembled of structural fragments containing these and unreacted hydroxyl and isocyanate groups and urethane groups. Relations for calculating the gel point, sol fraction, and concentration of elastically active network chains are derived. For a diol-diisocyanate system, two gel points are predicted: a sol-gel transition at a low excess of isocyanate and a gel-sol transition at a high excess. Critical excess of isocyanate groups and development of the gel were studied experimentally in systems composed of α,ω-dihydroxypoly(oxypropylene) and bis(4-isocyanatophenyl)methane at 60-140 °C. The reaction was catalyzed with dibutyltin dilaurate. Experimentally, the fractions of urea groups and of the sum of allophanate and biuret groups were determined by titration. The agreement with theory was good. At higher temperatures, an unknown side reaction not accounted for in the theory made the experimental gel fractions somewhat lower.

Introduction

The high reactivity of the isocyanate group is the reason for frequently occurring side reactions during or after the synthesis of polyurethanes or polyureas. These side reactions also include reactions with water and its reaction products. The most important reactions that may occur in hydroxyl-isocyanate systems are summarized in the following scheme:



By reaction of urethane with isocyanate, a trifunctional allophanate group is formed and another trifunctional group is formed by cyclotrimerization to give isocyanurate. Formation of the trifunctional groups promotes gelation and increases the cross-link density of the network. Traces of water are frequently present in polyols, particularly in commercial products. Since the molecular weight of water is low compared to that of the polyol, traces on the weight scale become nonnegligible on the molar scale. Upon splitting off of carbon dioxide, amine is formed, which readily reacts with isocyanate to give bifunctional urea groups. Formation of urea groups means chain extension. Formation of trifunctional biuret from urea and isocyanate also enhances cross-linking and gelation.

These side reactions occurring with isocyanate groups in excess are usually undesirable, particularly in the two-stage synthesis of polyurethanes since they lower the stability of the system after the first step, in which isocyanate-end-capped products are formed. However, cross-linking or additional cross-linking due to these "side" reactions is often intentional. Thus, optimum properties of polyurethanes are obtained with about 10% isocyanate groups in excess. Curing and/or manufacture of flexible foamed products is achieved by reaction with water. Cyclotrimerization to yield polyisocyanurates using special catalysts is often used in polyurethane coatings (cf., e.g., refs 1 and 2) and rigid foams.

In spite of the importance of side reactions for the modification of properties of polyurethanes, quantitative data on their intensity and particularly on their effect on network structure and properties are lacking.

The dependence of the intensity of these side reactions on the excess of NCO groups, temperature, concentration, and other factors was studied in model low-functional systems—monoalcohol-monoisocyanate-water. The reaction products were separated by HPLC and the components were identified.[3] Also, the investigation of gelation, sol fraction, and equilibrium elastic moduli of model networks prepared from poly(oxypropylene) triols and bis(4-isocyanatophenyl)methane with varying molar ratio of OH/NCO groups provided information about the importance of the side reactions.[4,5] The main conclusions of the studies, in which organotin compounds were used as catalysts, can be summarized as follows: (1) Side reactions always occur when isocyanate is in excess even with these selective catalysts. (2) Traces of water are important and contribute to network formation, formation of biuret is much faster than formation of allophanate, and also the equilibrium concentration of the former is higher. (3) The equilibrium concentration of biuret and allophanate decreases with increasing concentration; however, at lower temperatures (≤60 °C) the formation of biuret and allophanate is very slow.

Gelation in systems poly(oxypropylene) diol end capped with tolyldiisocyanate-butanediol was studied by Furukawa and Yokoyama.[6,7] They assumed allophanate formation as the only cross-linking reaction although they did not exclude reactions with traces of water present in the systems. The concentration of allophanate (and possibly of biuret) was determined by degradation with butylamine in dimethyl sulfoxide.

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In this paper, a theory of network formation due to side reactions based on the theory of branching processes is presented. The theoretical approach outlined elsewhere for some of the side reactions[8] has been modified and extended here. The calculation of the sol fraction has been modified, more fragments have been included, and possible variants in calculating the concentration of elastically active network chains have been examined. Network formation due to side reactions was studied in systems dihydroxypoly(oxypropylene)–bis(4-isocyanatophenyl)methane at 60–140 °C and the experimental sol fractions were compared with theoretical ones.

Experimental Section

Materials. α,ω-Dihydroxypoly(oxypropylene) (PPG 1200, Union Carbide Niax Polyol) was dried by azeotropic distillation with benzene. The concentration of hydroxyl groups was determined by reaction with phenyl isocyanate. The unreacted phenyl isocyanate was reacted with dibutylamine and its excess was determined by potentiometric titration with 0.3 M HCl using a combined glass electrode. PPG 1200 contained 2.68 wt % of hydroxyl groups; the number-average molecular weight determined by VPO, M_n, was 1230. The calculated number-average functionality, f_n, was 1.95. The content of water determined by coulometry was 0.0027 wt %.

Bis(4-isocyanatophenyl)methane (MDI) (Bayer) was purified by distillation at 180 °C and 270 Pa and then recrystallized from dry heptane. The purity of MDI determined by the reaction with dibutylamine and potentiometric titration was 99.5–99.7%.

Dibutyltin dilaurate (DBTDL) (Termolite T 12, M&T International) was used as received.

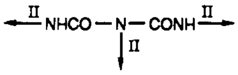
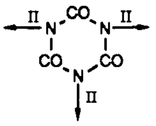
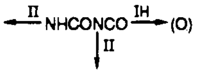
Preparation of Samples and Reaction Conditions. The samples of polyurethanes were prepared by reacting the components in sealed glass ampules in nitrogen atmosphere. The average mass of the samples was 0.5 g. Dibutyltin dilaurate was added as a 0.1 M solution in 1,4-dioxane; its amount (3 μL) corresponded to its mass concentration, 0.037–0.039 wt %. The reactions were stopped by cooling the sample down to −78 °C.

The reaction temperatures were 60, 90, 120, and 140 °C. Two kinds of dependences were studied: at constant composition and at constant time. The dependences on time were used for fixing the temperature at which steady values were obtained: 21 days at 90 °C, 5 days at 120 °C, and 4 days at 140 °C. The reaction time for the reference temperature of 60 °C, for which all OH groups and water molecules react but the extent of allophanate and biuret formation is negligible, was fixed at 5 days.

Determination of Unreacted Isocyanate Groups. The concentration of isocyanate groups in polyurethane samples was determined by the reaction with dibutylamine (DBA) and potentiometric titration of unreacted DBA with 0.3 M HCl in isopropyl alcohol. Polyurethane (about 0.5 g) was dissolved or swollen in 15 mL of 1,4-dioxane containing DBA at room temperature for about 12 h. The amount of DBA was chosen so as to keep the consumption of 0.3 M HCl below 3 mL. At a higher excess of DBA, there exists a danger of a partial decomposition of allophanate and biuret groups. Immediately before titration, the conductivity was raised by adding 7.5 mL of ethanol. Cross-linked swollen samples were titrated until a constant value was reached, i.e., up to several hours.

Determination of the Gel Fraction, w_g, and Critical Molar Ratio of NCO to OH Groups, r_{Ic}. The weight fractions of the gel in samples after determination of unreacted NCO groups, $(w_g)_{exp}$, were determined by repeated extraction with 1,4-dioxane for 3 weeks. The swollen gel was then dried to constant weight. The value $(w_g)_{exp}$ is higher than the sol fraction, w_g, by the weight of DBA reacted with the NCO groups. Since DBA reacts before extraction with NCO groups in both gel and sol, these data cannot be used directly for transformation of $(w_g)_{exp}$ into w_g. The fraction of free NCO groups in the gel was calculated by using the branching theory explained in the next section; the transformation formulas are given by eq 34 and 35.

Table I
Structural Fragments in the Polyurethane System Formed

unit	formula and types of bonds[a]	designation	mole fraction
isocyanate	$\xleftarrow{\text{II}}\text{NCO}$	R	r
urethane	$\xleftarrow{\text{II}}\text{NHCO}\xrightarrow{\text{IH}}\text{(O)}$	S	s
urea	$\xleftarrow{\text{II}}\text{NHCONH}\xrightarrow{\text{II}}$	T	t
biuret	 $\xleftarrow{\text{II}}\text{NHCO}-\underset{\downarrow\,\text{II}}{\text{N}}-\text{CONH}\xrightarrow{\text{II}}$	U	u
isocyanurate		X	x
allophanate	 $\xleftarrow{\text{II}}\text{NHCO}\underset{\downarrow\,\text{II}}{\text{N}}\text{CO}\xrightarrow{\text{IH}}\text{(O)}$	W	w
reacted hydroxyl	$\text{O}\xrightarrow{\text{HI}}$		α_H

[a] $\xrightarrow{XY}$ means a bond X→Y.

Results and Discussion

Branching Theory. The network formation in polyurethane systems, when only the urethane bonds are formed, is described in terms of the branching theory in a number of papers (cf., e.g., refs 4, 9, and 10). Of the side reactions, the effect of allophanate formation[11] and trimerization[12] was attacked first. The treatment of allophanate formation in ref 11 is based on the fact that an allophanate group is formed by coupling a reacted isocyanate group with a urethane group. Among the reacted isocyanate groups, those coupled with urethane groups were specially labeled and allowed to condense with an equal number of labeled urethane groups. This approach has the advantage that the total number of units during the process remains constant.

When, however, more groups are involved—such as allophanate, urea, biuret, isocyanurate—the labeling becomes too complicated. Therefore, the network has been built up from structural fragments as will be explained below. This approach has been outlined in ref 8. Here, it is generalized to include (a) the functionality distribution in polyol, (b) isocyanurate groups, and (c) calculation of the concentration of elastically active network chains. Also, the calculation of the sol fraction has been modified to take into account the actual weights of fragments instead of their average value.

The present approach is based on the theory of branching processes. The network is built up of the fragments listed in Table I.

These fragments are formed by the following reactions

$$\text{R} + \text{OH} \rightarrow \text{S}$$
$$\text{R} + \text{S} \rightarrow \text{W}$$
$$2\text{R} + \text{H}_2\text{O} \rightarrow \text{T}$$
$$\text{R} + \text{T} \rightarrow \text{U}$$
$$3\text{R} \rightarrow \text{X}$$

The sum of fractions of fragments is normalized to unity

$$r + s + t + u + w + x = 1 \qquad (1)$$

Let us assume that the polyol component is composed of molecules with different numbers of OH groups, given by their number fractions, n_i ($i = 1, 2, ...$; $\sum n_i = 1$).

In the theory of branching processes, the branched and cross-linked structures are generated from building units by proper combination of reacted functional groups or labeled points. The distribution of states of units with respect to the type and number of issuing bonds is described by the probability generating function (pgf) $\mathbf{F}_0$. An assumption is introduced at this point that the reactivity of OH groups in the polyol molecules (component H) is the same and independent; the same is assumed for the diisocyanate (this is valid, e.g., for MDI).

In this case, it is possible to take as building units monofunctional fragments obtained from the diisocyanate molecule by splitting it into two halves (Table I). Two types of bonds issuing from the isocyanate (I) fragments exist, I→I and I→H; the bonds issuing from polyol molecules are H→I. The pgf $\mathbf{F}_0$ has two components, F_{OH} and F_{OI} for the polyol and the isocyanate component, respectively

$$F_{\mathrm{OH}}(\mathbf{z}) = \sum n_i(1 - \alpha_{\mathrm{H}} + \alpha_{\mathrm{H}} z_{\mathrm{HI}})^i \qquad (2)$$

$$F_{\mathrm{OI}}(\mathbf{z}) = (r + s z_{\mathrm{IH}} + t z_{\mathrm{II}} + u z_{\mathrm{II}}^2 + w z_{\mathrm{IH}} z_{\mathrm{II}} + x z_{\mathrm{II}}^2) z_{\mathrm{II}} \qquad (3)$$

where $\mathbf{z} = (z_{\mathrm{II}}, z_{\mathrm{IH}}, z_{\mathrm{HI}})$ and the components of the vector $\mathbf{z}$ are auxiliary variables of the pgf's; the prefactor at $z_{\mathrm{KL}}{}^m$ is equal to the probability of finding a fragment issuing m oriented bonds K→L; α_{H} is the molar conversion of hydroxyl groups. The other symbols are defined in Table I. The probability generating function for the types and numbers of bonds issuing from units in generation $g > 0$ depends for a unit of type I on the type of bond it is connected to the unit in generation $g - 1$ with

$$F_{\mathrm{IH}}(\mathbf{z}) = \sum i n_i(1 - \alpha_{\mathrm{H}} + \alpha_{\mathrm{H}} z_{\mathrm{HI}})^{i-1} / \sum i n_i \qquad (4)$$

$$F_{\mathrm{HI}}(\mathbf{z}) = (s + w z_{\mathrm{II}}) z_{\mathrm{II}} / (s + w) \qquad (5)$$

$$F_{\mathrm{II}}(\mathbf{z}) = (r + s z_{\mathrm{IH}} + t z_{\mathrm{II}} + u z_{\mathrm{II}}^2 + w z_{\mathrm{II}} z_{\mathrm{IH}} + x z_{\mathrm{II}}^2 + z_{\mathrm{II}}(t + 2u z_{\mathrm{II}} + w z_{\mathrm{IH}} + 2x z_{\mathrm{II}})/(r + s + 2t + 3u + 2w + 3x) \qquad (6)$$

where $F_{\mathrm{XY}}(\mathbf{z})$ means a pgf for a unit rooted in generation $g - 1$ through the bond Y→X.

The gel point is given by the condition that the determinant D is equal to zero

$$D = \det(\delta_{\mathrm{IJ}}{}^{\mathrm{KL}} - F_{\mathrm{IJ}}{}^{\mathrm{KL}}) = 0 \qquad (7)$$

where $\delta_{\mathrm{IJ}}{}^{\mathrm{KL}}$ is the Kronecker δ equal to 1 for IJ = KL and zero otherwise and $F_{\mathrm{IJ}}{}^{\mathrm{KL}} = (\partial F_{\mathrm{IJ}}/\partial z_{\mathrm{KL}})_{z=1}$. Equation 7 yields the following expression

$$[3(x + u) - (r + s)](s + w) + \alpha_{\mathrm{H}}(f_{\mathrm{Hw}} - 1)(s + 2w)^2 = 0 \qquad (8)$$

where $f_{\mathrm{Hw}} = \sum i^2 n_i / \sum i n_i$.

In the experimental system discussed below, the poly(oxypropylene) diol contained a small admixture of the monofunctional component, so that $\sum n_i = n_1 + n_2 = 1$ and eq 8 is transformed into

$$[3(x + u) - (r + s)] + 2\alpha_{\mathrm{H}} n_2 (s + 2w)^2/(n_1 + 2n_2)(s + w) = 0 \qquad (9)$$

The key quantities beyond the gel point are the extinction probabilities v_{KL}; i.e., v_{KL} is the probability that the bond K→L has finite continuation. The extinction probabilities are given by the following expressions:

$$v_{\mathrm{IH}} = F_{\mathrm{IH}}(v_{\mathrm{HI}}) = [n_1 + 2n_2(1 - \alpha_{\mathrm{H}} + \alpha_{\mathrm{H}} v_{\mathrm{HI}})]/(n_1 + 2n_2) \qquad (10)$$

$$v_{\mathrm{HI}} = F_{\mathrm{HI}}(v_{\mathrm{II}}) = (s + w v_{\mathrm{II}}) v_{\mathrm{II}}/(s + w) \qquad (11)$$

$$v_{\mathrm{II}} = F_{\mathrm{II}}(v_{\mathrm{II}}, v_{\mathrm{IH}}) = [r + s v_{\mathrm{IH}} + t v_{\mathrm{II}} + u v_{\mathrm{II}}^2 + w v_{\mathrm{II}} v_{\mathrm{IH}} + x v_{\mathrm{II}}^2 + v_{\mathrm{II}}(t + 2u v_{\mathrm{II}} + w v_{\mathrm{IH}} + 2x v_{\mathrm{II}})]/(r + s + 2t + 3u + 2w + 3x) \qquad (12)$$

The sol is composed of units having no bonds with infinite continuation. The weight of these units, A, is given by the expression

$$A = [N_{\mathrm{R}} M_{\mathrm{R}} v_{\mathrm{II}} + N_{\mathrm{S}} M_{\mathrm{S}} v_{\mathrm{II}} v_{\mathrm{IH}} + N_{\mathrm{T}} M_{\mathrm{T}} v_{\mathrm{II}}^2 + N_{\mathrm{U}} M_{\mathrm{U}} v_{\mathrm{II}}^3 + N_{\mathrm{W}} M_{\mathrm{W}} v_{\mathrm{II}}^2 v_{\mathrm{IH}} + N_{\mathrm{X}} M_{\mathrm{X}} v_{\mathrm{II}}^3 + N_{\mathrm{H}} M_{\mathrm{H}} v_{\mathrm{HI}}(n_1 + n_2 v_{\mathrm{HI}})] \qquad (13)$$

where N_{K} is the number of moles of the fragment K and M_{K} is its molecular weight.

The weight fractions of the sol, w_{s}, and gel, w_{g}, are given by the expression

$$w_{\mathrm{s}} = 1 - w_{\mathrm{g}} = A/B \qquad (14)$$

where B is the weight of the whole system

$$B = N_{\mathrm{R}} M_{\mathrm{R}} + N_{\mathrm{S}} M_{\mathrm{S}} + N_{\mathrm{T}} M_{\mathrm{T}} + N_{\mathrm{U}} M_{\mathrm{U}} + N_{\mathrm{W}} M_{\mathrm{W}} + N_{\mathrm{X}} M_{\mathrm{X}} + N_{\mathrm{H}} M_{\mathrm{H}} \qquad (15)$$

The sol fraction, w_{s}, can be also expressed through the fractions of fragments r, s, t, u, w, and x. For this purpose, the expressions for A and B (eqs 13 and 14) are divided by the sum

$$S_1 = N_{\mathrm{R}} + N_{\mathrm{S}} + N_{\mathrm{T}} + N_{\mathrm{U}} + N_{\mathrm{W}} + N_{\mathrm{X}}$$

and for N_{H}/S_1 one gets

$$\frac{N_{\mathrm{H}}}{S_1} = \frac{N_{\mathrm{H}}}{f_{\mathrm{Hn}} N_{\mathrm{H}}} \frac{f_{\mathrm{Hn}} N_{\mathrm{H}}}{S_2} \frac{S_2}{S_1}$$

where

$$S_2 = N_{\mathrm{R}} + N_{\mathrm{S}} + 2M_{\mathrm{T}} + 3N_{\mathrm{U}} + 2N_{\mathrm{W}} + 3N_{\mathrm{X}}$$

so that

$$S_2/S_1 = r + s + 2t + 3u + 2w + 3x$$

and

$$f_{\mathrm{Hn}} N_{\mathrm{H}}/S_2 = 1/r_{\mathrm{I}} = [\mathrm{OH}]_0/[\mathrm{NCO}]_0$$

where f_{Hn} is the number-average functionality of component H. Using these relations, one gets for w_{s}

$$w_{\mathrm{s}} = A'/B' \qquad (16)$$

where

$$A' = r M_{\mathrm{R}} v_{\mathrm{II}} + s M_{\mathrm{S}} v_{\mathrm{II}} v_{\mathrm{IH}} + t M_{\mathrm{T}} v_{\mathrm{II}}^2 + u M_{\mathrm{U}} v_{\mathrm{II}}^3 + w M_{\mathrm{W}} v_{\mathrm{II}}^2 v_{\mathrm{IH}} + x M_{\mathrm{X}} v_{\mathrm{II}}^3 + (1/f_{\mathrm{Hn}} r_{\mathrm{I}})(S_2/S_1) M_{\mathrm{H}}(n_1 + n_2 v_{\mathrm{HI}}) v_{\mathrm{HI}}$$

$$B' = r M_{\mathrm{R}} + s M_{\mathrm{S}} + t M_{\mathrm{T}} + u M_{\mathrm{U}} + w M_{\mathrm{W}} + x M_{\mathrm{X}} + (1/f_{\mathrm{Hn}} r_{\mathrm{I}})(S_2/S_1) M_{\mathrm{H}}$$

Under experimental conditions, the sol fraction is determined after deactivation of the unreacted isocyanate groups with dibutylamine. Thus the experimentally determined $w_{\mathrm{s,exp}}$ is higher than the calculated one by the amount of reacted dibutylamine units. This difference will be derived in the next section.

The concentration of elastically active network chains (EANC), which determine the equilibrium elasticity of the gel, is usually derived from the number of elastically active cross-links (EAC). An elastically active cross-link is a junction in the network structure from which at least three paths issue to infinity. Each bond with infinite continuation issuing from this EAC contributes one-half to the number of EANC's.

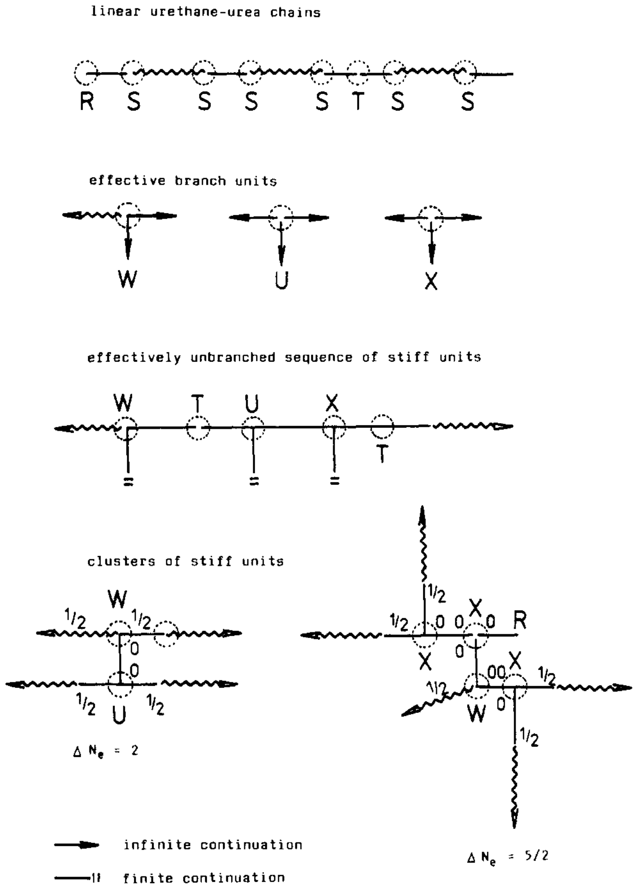


Figure 1. Sketch of a cluster of stiff units and counting of elastically active network chains (EANC): (—) stiff connection in MDI; (﹏) flexible elastomeric chain; the figures denote the contribution to the number of EANC's.

In terms of the fragments listed in Table I, the biuret (U), allophanate (W), and isocyanurate (X) fragments can contribute to the number of EANC's. Then the number of EANC's per building unit (fragments and polyol molecules), N_e, is given by the folllowing relation

$$N_e = (3/2)n_{fr}[u(1 - v_{II})^3 + w(1 - v_{II})^2(1 - v_{HI}) + x(1 - v_{II})^3] \quad (17)$$

The number fraction of fragments, n_{fr}, is given by the relation

$$n_{fr} = \frac{N_{fr}}{N_{fr} + N_H} = (N_R + N_S + N_T + N_U + N_W + N_X)/(N_R + N_S + N_T + N_U + N_W + N_X + N_H) \quad (18)$$

where N_{fr} is the number of I fragments, N_K is the number of K fragments, and N_H is the number of polyol molecules. The number of isocyanate units in all fragments, N_I, is given by the relation

$$N_I = (r + s + 2t + 3u + 2w + 3x)N_{fr} \quad (19)$$

which gives for n_{fr} the following relation:

$$n_{fr} = N_I/[N_I + (r + s + 2t + 3u + 2w + 3x)N_H] \quad (20)$$

The number of moles of OH groups $\mathcal{N}_H = N_H(2n_2 + n_1)$, so that eq 20 written in terms of the initial molar ratio $r_I = [NCO]_0/[OH]_0$ eventually yields

$$n_{fr} = r_I/[r_I + (r + s + 2t + 3u + 2w + 3x)/2(n_1 + 2n_2)] \quad (21)$$

Equation 17 is expected to be valid for a network where the number of groups formed by side reactions is small compared to the number of urethane groups. Then the probability of finding a urethane unit, i.e., also an elastomeric chain, next to a branch point (allophanate, biuret, isocyanurate) is close to unity and all three branches of such a junction contribute to the number of EANC's.

If the concentration of "stiff" isocyanate fragments is higher, the expected number of EANC's is lower because some of the sequences considered as EANC's, according to reasoning given above, are relatively short and formed of "stiff" units. Such a situation is depicted in Figure 1. A bond with infinite continuation issuing from an EAC is to be considered effective only if the sequence it starts proceeds, possibly via an *effectively unbranched sequence* of stiff units, to an elastomeric element that is bound to a urethane unit. If it proceeds to an EAC, the contribution is zero. An effectively unbranched sequence is composed of units having two and only two bonds with infinite continuation.

The probability of finding a stiff unit belonging to an effectively unbranched sequence is derived from the probabilities of finding units in a sequence with infinite continuation. For this purpose, the following substitution of variables z in the pgf $F_{OI}(\mathbf{z})$ is made

$$z_{IH} \rightarrow v_{IH} + (1 - v_{IH})z$$
$$z_{II} \rightarrow v_{II} + (1 - v_{II})z$$

where z is now associated with bonds having continuation to infinity. A sequence with infinite continuation can be composed of units with two or more (three in our case) bonds with infinite continuation. Their fractions correspond to the coefficients at z^2 or z^3:

fragments in stiff sequence	
urea	$t_2 = t(1 - v_{II})^2$
biuret	$u_2 = 3u(1 - v_{II})^2 v_{II}$
allophanate	$w_2 = w(1 - v_{II})^2 v_{IH}$
isocyanurate	$x_2 = 3x(1 - v_{II})^2 v_{II}$
fragments starting a flexible sequence	
urethane	$s_{11} = s(1 - v_{II})(1 - v_{IH})$
allophanate	$w_{11} = 2w(1 - v_{II})(1 - v_{IH})v_{II}$
elastically active branch points	
biuret	$u_3 = u(1 - v_{II})^3$
allophanate	$w_3 = w(1 - v_{II})^2(1 - v_{IH})$
isocyanurate	$x_3 = x(1 - v_{II})^3$

The probability that any of these units occurs in the infinite path of units connected by II bonds is proportional to its fraction and to the number of II bonds it is engaged in.

Therefore, an effectively unbranched sequence of any length (from 0 to ∞) is ended by a unit from that an elastomeric chain starts with the probability Ψ_1

$$\Psi_1 = N_i^{-1}(s_{11} + w_{11}) \quad (22)$$

and the probability that the sequence is ended by an EAC, Ψ_2, is given by

$$\Psi_2 = N_i^{-1}(3u_3 + 3w_3 + 3x_3) \quad (23)$$

where

$$N_i = 2t_2 + 2u_2 + 2w_2 + 2x_2 + s_{11} + w_{11} + 3u_3 + 3w_3 + 3x_3 \quad (24)$$

The quantity Υ

$$\Upsilon = 1 - \Psi_1 - \Psi_2 = N_i^{-1}(2t_2 + 2u_2 + 2w_2 + 2x_2) \quad (25)$$

is the probability that a unit of the stiff effectively unbranched sequence is a part of a path with infinite continuation. Since one has to consider sequences of any length, the probability of the existence of sequences of any length, Ω, is obtained by summation

$$\Omega = \sum_{i=0}^{\infty} \Upsilon^i = 1/(1 - \Upsilon) = 1/(\Psi_1 + \Psi_2) \quad (26)$$

Therefore, an II bond with infinite continuation is counted as contributing to the number of EANC's with the probability $\Omega\Psi_1$ and is not counted with the probability $\Omega\Psi_2$.

On the basis of these considerations, the enumeration generating function for the number of bonds issuing from EAC's and contributing to the number of EANC's, $T(z)$, can be formulated as follows:

$$T(z) = (u_3 + x_3)(1 - \Omega\Psi_1 + \Omega\Psi_1 z)^3 + w_3 z(1 - \Omega\Psi_1 + \Omega\Psi_1 z)^2 \quad (27)$$

The number of EANC's per building unit (fragments and polyol molecules), N_e, is then given by

$$N_e = (1/2)n_{fr}[\partial T(z)/\partial z]_{z=1} = (1/2)n_{fr}[3\Omega\Psi_1(u_3 + x_3) + (1 + 2\Omega\Psi_1)w_3] \quad (28)$$

The concentration of EANC's per unit weight of the whole system (including sol), ν_e, is given by

$$\nu_e = N_e/M_u \quad (29)$$

per unit weight of the gel, ν_{eg}, it reads

$$\nu_{eg} = N_e/M_u w_g \quad (30)$$

where M_u is the number-average molecular weight of the building unit

$$M_u = n_{fr}(rM_R + sM_S + tM_T + uM_U + wM_W + xM_X) + (1 - n_{fr})\sum n_i M_i \quad (31)$$

and n_i and M_i refer to the polyol molecules.

Model Systems. Conditions for gelation and changes in the sol fraction and concentration of EANC's can be calculated by using the theory developed above. Two sets of input data can be used: (1) distribution of fragments determined analytically; (2) set of rate constants characterizing the elementary reaction steps from which the distribution of fragments can be calculated. Unfortunately, constants characterizing the complete kinetic scheme in polymer systems are not available at present, neither are reliable methods for a complete analysis. It will be shown below how an incomplete set of analytical data can be utilized with the help of the branching theory.

Figures 2 and 3 demonstrate the effect of changes in the composition on the sol fraction and concentration of EANC's. In Figure 2, results are shown for a water-free system in which allophanate formation is the only side reaction, i.e., $t = u = x = 0$. The sol fraction and concentration of EANC's are plotted against the ratio $r_I = [NCO]_0/[OH]_0$ and it is assumed that the concentration of allophanate groups is governed by the equilibrium

$$K_W = w/sr \quad (32)$$

It is seen that two gel points are predicted when the excess of isocyanate is increased—a sol → gel transition at a low excess of diisocyanate and a gel → sol transition at a high excess of isocyanate. In the former case, a few branch points introduced into a system of linear chains cause gelation, whereas in the latter case the branches in a relatively highly branched system are terminated by unreacted isocyanate groups.

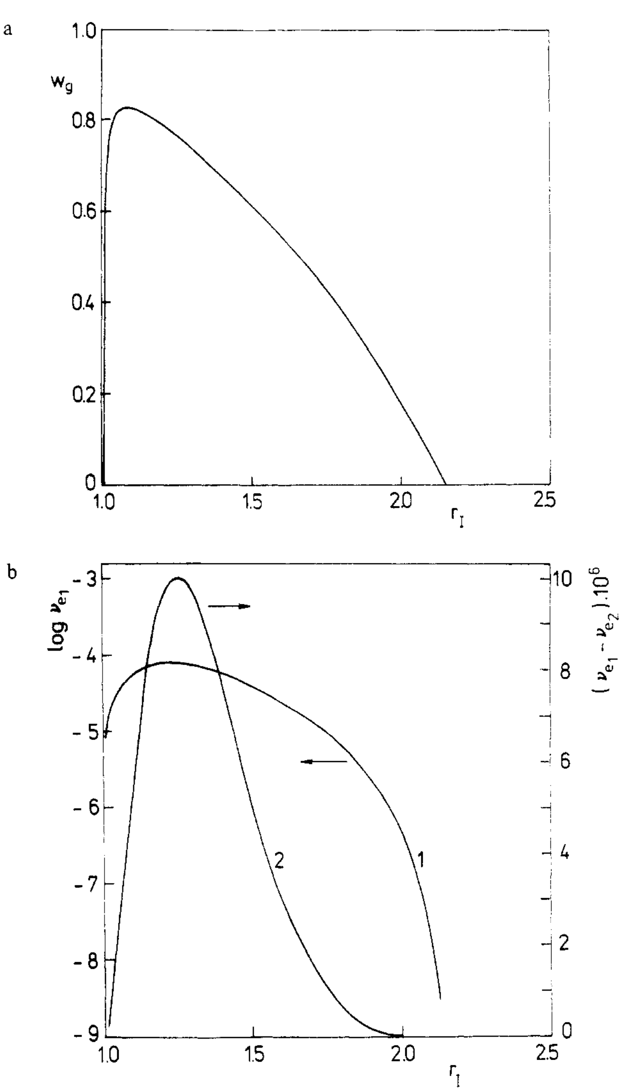


Figure 2. Calculated dependence of the gel fraction, w_g (a), and concentration of EANC's, ν_e (b) on the molar ratio r_I caused by allophanate formation: $\alpha_H = 0.99$, $K_W = 1.0$. (b) Curve 1, ν_{e1} contributed by all elastically active branch points, eq 17; curve 2, the difference between ν_{e1} and ν_{e2} in which the existence of stiff clusters is taken into account, eq 28.

The concentration of EANC's passes through a maximum corresponding to the minimum of w_s. The two theoretical approaches—one disregarding the existence of stiff structures and the other taking their existence into account—give practically the same results at low excess of isocyanate, i.e., a low extent of side reactions. However, the difference between the two curves also decreases at low cross-linking densities at a high excess of isocyanate when the gel → sol transition is approached. This feature is caused by the fact that only a few elastically active branch points (i.e., those from which three paths issue to infinity) exist in the system, so that a state is approached where one elastically active branch point is contained in one (possibly large) stiff cluster. In the region of the highest cross-linking densities (maximum w_g), the two curves differ by a factor of ~2, i.e., about 50% of the elastically active branch points are buried in the stiff structures.

The other examples given in Figure 3 demonstrate the effect of variation in the structure of the branch points.

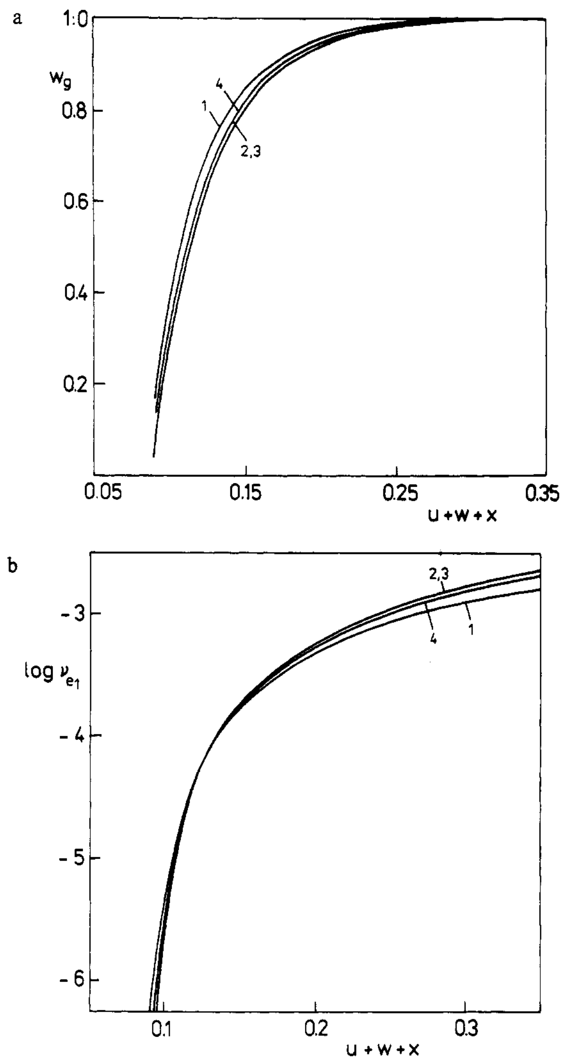


Figure 3. Effect of the structure of the branch point on the calculated values of w_g (a) and ν_{e1} (b, mol/L, eq 17). All curves, $s = 0.5$, $t = 0.15$, $r = 1 - s - t - u - w - x$; curve 1, $u = x = 0$, w varies; curve 2, $w = x = 0$, u varies; curve 3, $u = w = 0$, x varies; curve 4, u:w:x = 1:1:1.

The branch points are formed either by allophanate, biuret, or isocyanurate groups and the fraction of bifunctional urea and urethane group is kept constant or varies only little. It can be seen that neither the sol fraction nor the concentration of EANC's differ much when plotted against the sum $u + w + x$. This result suggests that one can treat theoretically also systems where the exact proportion between the branch points of different nature is not known.

Comparison with Experiments. Experimentally, gelation due to side reactions in systems composed of α,ω-dihydroxypoly(oxypropylene) and bis(4-isocyanatophenyl)methane was studied at 60, 90, 120, and 140 °C. Dibutyltin dilaurate was used as a catalyst.

Unfortunately, reliable analytical methods for polyurethane systems that are able to distinguish between various structural fragments do not exist. When various fragments occur in the system simultaneously, IR or NMR spectra are too complex and the amine degradation is not specific (for instance, it cannot distinguish between allophanate and biuret groups). Therefore, in this study we made use of the knowledge about relative reaction rates of individual reaction steps and equilibria between fragments accumulated in the study of side reactions in low-functionality systems in ether solvents modeling the systems of the present study.[3]

The following conclusions can be made from the model studies corresponding to the same concentrations of groups, temperature range, and catalyst concentrations:

(a) Urethane formation is the fastest reaction and the conversion of OH groups (minority groups) is practically complete (~98–99%).

(b) Under the given experimental conditions, isocyanurate is not formed.

(c) Reaction with water with formation of urea groups is the second fastest reaction. At 60 °C and reaction times of 5 days, water reacted completely and formation of allophanate and biuret is negligible, so that only unreacted isocyanate, urethane, and urea groups were found in the system.

(d) At higher temperatures, formation of only biuret and allophanate groups is detected.

(e) During dissolution or swelling of polyurethane samples in dioxane solutions of dibutylamine (used for determination of unreacted NCO groups) at room temperature, neither urethane and urea nor allophanate and biuret groups are split.

From these finding, the initial composition of the system, and the experimentally determined concentration of unreacted NCO groups, the sum of fractions of allophanate and biuret groups and the fractions of other fragments can be calculated. The following mass balance is used:

$$\begin{aligned} 2[\mathrm{T}]_0 &= [\mathrm{R}]_0 - [\mathrm{H}]_0 - [\mathrm{R}]_{60} \\ [\mathrm{T}]_0 &= [\mathrm{T}]_{60} = [\mathrm{T}] - [\mathrm{U}] \\ [\mathrm{S}]_0 &= [\mathrm{H}]_0 = [\mathrm{S}] + [\mathrm{W}] \\ [\mathrm{R}]_{60} &= [\mathrm{R}] + ([\mathrm{U}] + [\mathrm{W}]) \\ [\mathrm{X}] &= 0 \end{aligned} \tag{33}$$

$[\mathrm{R}]_0$ and $[\mathrm{H}]_0$ are the initial concentrations of NCO and OH groups, respectively; the subscript 60 means the concentration of the rerspective fragments after the reaction at 60 °C. The value of $[\mathrm{T}]_{60}$ was obtained from the initial conditions and concentration of unreacted isocyanate groups after the reaction at 60 °C. The difference in the concentration of NCO groups at 60 °C and higher reaction temperatures corresponds to the formed allophanate and biuret groups. The dependences of the composition of these systems on temperature and time prior to and beyond the gel point have been published elsewhere.[13]

The gel fraction w_g was the structural parameter offered by the theory that was also determined experimentally. The dependence of w_g on the molar ratio r_I for temperatures of 90, 120, and 140 °C is shown in Figure 4. The data correspond to sufficiently long reaction times after which the gel fraction no longer changed. In agreement with the results of model experiments, at 60 °C and after 5 days no gel was formed. Also, no biuret or allophanate groups were found by the amine degradation method[6] after these or longer reaction times.

As pointed out in the theoretical section, the experimental gel fraction differs from the calculated one because in experiment the unreacted NCO groups were deactivated before determination of the gel fraction by addition of dibutylamine. Therefore, the contribution by the reacted dibutylamine, Δ_A, is to be subtracted

$$w_s = w_{s,\mathrm{exp}} - \Delta_A \tag{34}$$

The contribution Δ_A is proportional to the number of moles of NCO groups in the gel, $n_{I,g}$, per number-average weight of the building unit multiplied by the molec-

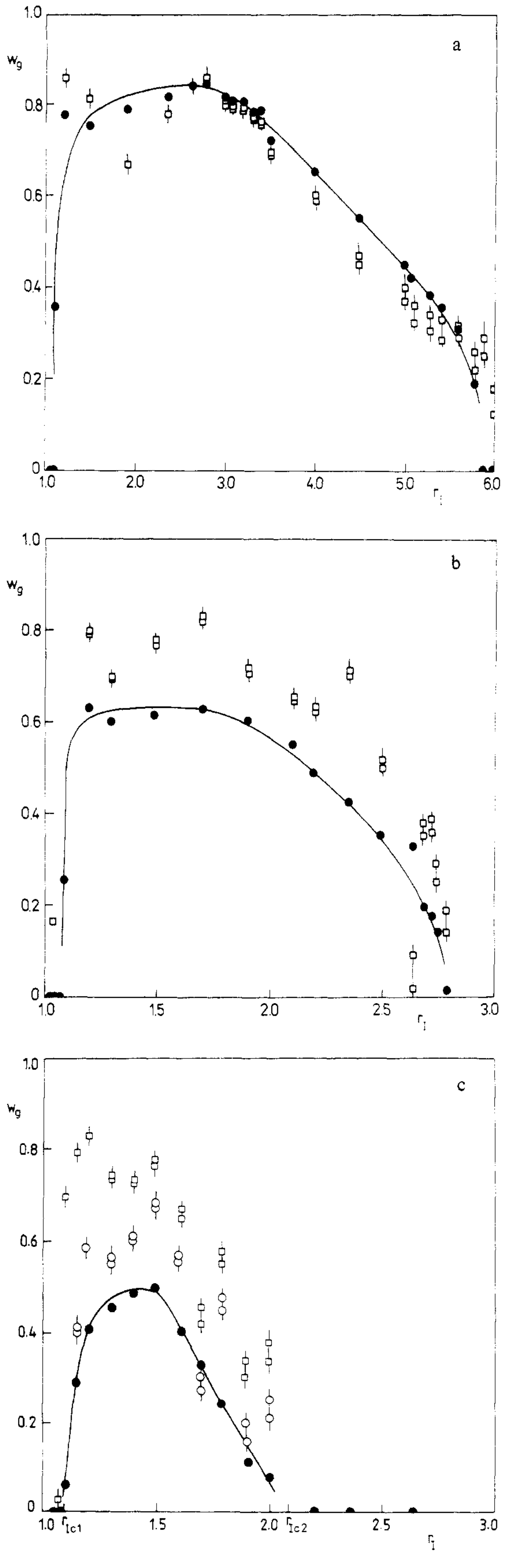


Figure 4. Gel fraction in the systems dihydroxypoly(oxypropylene)-bis(4-isocyanatophenyl)methane (MDI) as a function of the initial molar ratio of NCO to OH groups, r_I, after long reaction times. Temperature in °C: (a) 90, (b) 120, (c) 140. (●) Experimental data; (—) interpolated experimental dependence; (○, □) the two extremes of calculated values for maximum biuret or allophanate formation for α_H = 0.96 and 1.0, respectively.

Table II
Critcal Molar Ratios of NCO to OH Groups, r_{Ic}, Necessary for Gelation

temp, °C	reactn time,[a] days	$r_{Ic}(s \rightarrow g)$	$r_{Ic}(g \rightarrow s)$
90	21	1.08	5.9
120	5	1.08	2.8
140	4	1.08	2.1

[a] The reaction time corresponds to steady-state concentrations of groups.

ular weight of dibutylamine. The number of moles $n_{I,g}$ is given by

$$\Delta_A = M_{DBA}N_R(1 - v_{II})/B = r_I(1 - v_{II})/B' \qquad (35)$$

because an isocyanate fragment must be connected with the gel through one II bond with infinite continuation (cf. also eqs 14 and 16).

As predicted by the theory, two gel points were found corresponding to two critical values of r_I, r_{Ic} for the sol → gel (s → g) and gel → sol (g → s) transitions, respectively (Table II). The position of the s → g transition is practically independent of temperature but the other one decreases with increasing temperature. Also the maximum content of the gel, $w_{g,max}$, decreases with increasing temperature. Therefore, with increasing temperature the region where gel exists becomes smaller. This is in line with decreasing stability of allophanate and biuret.

The calculation of the sol fraction by using the branching theory is somewhat hampered by the fact that one knows only the sum of allophanate and biuret groups. Therefore, two possible extremes were considered for the transformation of isocyanate, reacted in excess, to urethane and urea: (1) 100% formation of allophanates, i.e., $[U] = 0$, $[T] = [T]_{60}$, and $[W] = [R]_{60} - [R]$; (2) maximum formation of biuret groups, i.e., $[T] = 0$, $[U] = [T]_{60}$, and $[W] = [R]_{60} - [R] - [T]_{60}$ if $[R]_{60} - [R] > [T]_{60}$ and $[T] = [T]_{60} - ([R]_{60} - [R])$ and $[W] = 0$ if $[R]_{60} - [R] < [T]_{60}$.

The results in Figure 4 show that the difference between these two extremes is in most cases not large. The agreement between the theory and experiments for systems reacted at 90 °C is good. At 120 and 140 °C, the theoretical values of w_g are higher than the experimental ones. In the calculations, it has been assumed that the conversion of OH groups $\alpha_H = 1$ and that no ring formation takes place. In reality, α_H may drop to 0.98 and the number of bonds that are elastically inactive may, for this system, amount to up to 2% in conversion,[14] so that the effective conversion to intermolecular bonds may drop to 0.96. Figure 4c for reaction at 140 °C shows that the theoretical values of w_g do not decrease enough to reach an agreement with experiments. Moreover, a decrease of conversion and increase in cyclization with increasing temperature would be hard to explain.

Therefore, we assume that the lowering of w_g compared to the theoretical values is due to some additional reaction in which the isocyanate groups are consumed but not involved in formation of (intermolecular) bonds. Alternatively, the difference between the calculated and theoretical values of w_g in combination with the branching theory can be used for calculation of the amount of deactivated isocyanate groups. It is assumed that they form a monofunctional inactive product. It comes out that on average 1.5% of the initial value of $[R]_0$ is enough to explain the observed difference.

Because of the low extent of the deactivation reaction, it is not surprising that the corresponding products were not identified in model experiments.[3] However, even in the model reactions at higher temperatures some trace amounts of unidentified products were observed in the HPLC records. Their UV response corresponded to up to 5% of the total absorption, which may well have included the product of the assumed deactivation reaction.

Conclusions

The network formation theory, based on the theory of branching processes, in which branched and cross-linked structures are assembled from structural fragments, seems to describe well real systems composed of a macrodiol and diisocyanate. The two gel points corresponding to sol → gel and gel → sol transitions predicted by the theory were observed experimentally. With increasing temperature, the latter transition is shifted to a lower excess of isocyanate groups and the region where the gel exists becomes narrower. This is due to a decrease in stability of allophanate and biuret groups. At higher temperatures, the experimental gel fractions are smaller than the theoretical ones. This fact is explained by some unidentified side reaction in which NCO groups are deactivate but their intensity is rather low.

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Comparative Study on the Folded-Chain Structure in Polyethylene and Cycloparaffins. 1. TEM Study on Molecular Orientation of Polyethylene on a Decorated Surface of Polyethylene and Cycloparaffin Single Crystals

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ABSTRACT: The folded-chain structure of polyethylene (PE) was compared with that of cycloparaffins by using the vapor-deposition method of PE on the fold surface of their single crystals. The vapor-deposited PE molecules orient in the direction parallel to the *b*-axis of monoclinic cycloparaffins, $(CH_2)_{36}$ and $(CH_2)_{60}$, which is parallel to the "folding direction". When the fold surface of a PE single crystal was decorated as above, the deposited PE molecules orient parallel to the (110) growth face in each (110) sector of the single crystal. This fact strongly supports the (110) fold in the (110) sector of PE single crystal. Decoration with vapor-deposited PE on the surface of a lozenge-shaped single crystal of orthorhombic cycloparaffin, $(CH_2)_{120}$, also showed identical morphology to the case of a PE single crystal. This fact evidences the (110) fold of the $(CH_2)_{120}$ crystal, although there still remains the question whether the fold structure of $(CH_2)_{120}$ is the same as that of PE. The orientational relationship between the deposited PE and various substrates is also discussed by analyzing their electron diffraction patterns. For example, the 002 reflection from deposited PE was arced for PE and $(CH_2)_{120}$ substrates, but it was not arced for $(CH_2)_{36}$ and $(CH_2)_{60}$ substrates. This result suggests that there exists some orientational distribution of the molecular axis of PE deposited on PE and $(CH_2)_{120}$ single crystals.

1. Introduction

The folded-chain structure of polyethylene (PE) has been studied extensively, since it was found in the single crystals grown from a solution in 1957.[1] Some models of the structure were proposed: regular sharp fold model, loose loop model, and random reentry model.[2] It is the current belief that the folded-chain structure is somewhat regular,[3,4] which means adjacent reentry, although there still remain problems, such as distribution in the folding direction and the size of fold parts.

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