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(44) Radii of gyration, R_g, in the good solvent THF were assumed to approximate those in benzene for which a relationship between R_g and M is given in ref. 25. R_g values in cyclopentane were assumed to equal those in cyclohexane, from the relationship in ref 38. R_g values in ethyl acetate are obtained by assuming equality with dimensions in another marginal solvent, di-*n*-butyl phthalate.[42] The R_g values lay in the ratio 1:0.85:0.44. These R_g data were used to estimate approximate overlap concentrations from $C^* = 3M/\pi R_g{}^3 N_A$.

Monte Carlo Simulation of the Formation of Irregular Structures in Poly(vinyl chloride)

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ABSTRACT: The Monte Carlo simulation of the formation of structural defects is carried out with microcomputers programmed in Basic. It is based on the most recent data for the polymerization mechanism and allows an interpretation of structural defects before and after the pressure drop. The deficiency in our knowledge of the mechanisms is pointed out, and some suggestions to fill the gap are discussed.

Introduction

The mechanism of the thermal degradation of poly(vinyl chloride) (PVC) is not yet fully clarified;[1-3] however, because it was shown in early work that the model compounds for the regular structures of PVC, such as the various isomers of 2,4-dichloropentane and 2,4,6-trichloroheptane, are thermally stable at the processing temperature, it is generally believed that the irregular structures—especially allylic and tertiary chlorides—are related to the initiation of the unzippering dehydrochlorination process. Consequently, the physicochemical analysis of these defects and the mechanism of their generation have been research objectives for a long time. Following the use of sophisticated NMR methods[4-6] as well as the formation of a 5 year cooperative IUPAC working party devoted to that subject,[7,8] major progress has been achieved recently for the first objective, although quantitative agreement between the results of ^{1}H NMR[8] and ^{13}C NMR[5] on the same samples is not totally satisfactory. On the other hand, assessing the importance of the head-to-head propagation mechanism, followed by isomerization and possible decomposition of the resulting radical, gave the key for understanding the main-chain end formation. In addition, most of the branching mechanisms that involve the transfer of the growing radical onto the polymer are also now understood. It then becomes possible, by assuming quantitative probabilities for the various products of these two basic mechanisms, to simulate the generation of the polymer molecules with their structural defects and chain ends.

Basic Features of the Simulation

The defects involved here are the chain ends, the branches and their associated branch points and ends, and the unsaturated structures, both at the chain ends and along the polymer backbone. The oxygenated structures coming from the byproducts of the reactions of accidental traces of oxygen are not considered here.

As for the chain ends, it has long been considered that, in addition to the radical-generated residues, they are produced by a transfer mechanism to the monomer; the transfer constant to the monomer is very large, 1.1×10^{-3} at 50 °C,[9] 10 times larger than the value expected for the reactivity of the poly(vinyl chloride) radical—which is similar to that of the poly(vinyl acetate) radical—or of the monomer structure, which might be compared to that of acrylonitrile. The corresponding transfer constants to the monomer are 2×10^{-4} for vinyl acetate and 1.7×10^{-5}[10] for acrylonitrile. The expected structures resulting from the possible mechanism of monomer transfer are shown in Scheme I. None of the unsaturated chain ends expected from this scheme have actually been observed with

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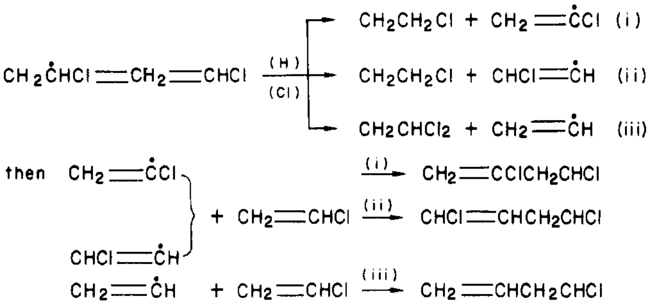
Scheme I

Expected Chain Ends from Transfer on the Vinyl Chloride Monomer



the most advanced NMR methods; the same is true for the saturated structure (iii) resulting from the transfer of a chlorine atom. For this reason, the mechanisms shown in Scheme I will not be considered in the computer simulation.

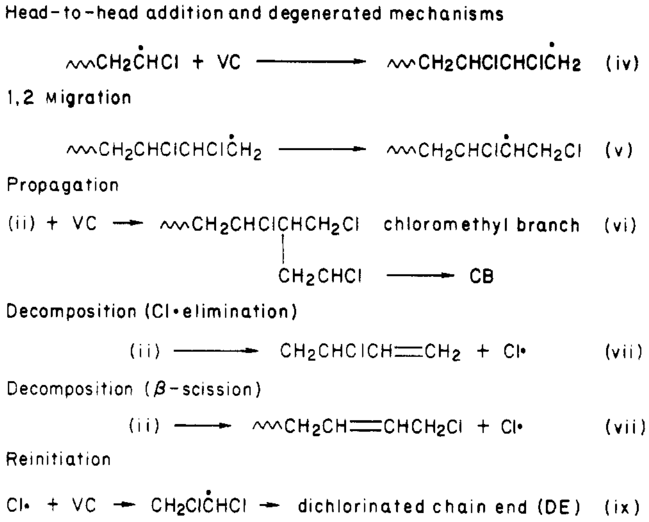
The amount of radical-generated residues in PVC is very small. In a low molecular weight extract of a commercial polymer prepared with a percarbonate initiator, Van der Heuvel et al.[6] only found 0.8 carbonate residue per 1000 monomer unit. By comparison, the number of unsaturated chain ends was about 10 times higher (8.6). If the amount of initiator residue in the whole polymer is the same as in the low molecular weight extract, it should be of the order of 0.4 residue per chain. However, it is clear that the actual value is certainly lower, and indeed initiator residues in the whole polymer have not been detected in all the work of the IUPAC working party. More recently, Starnes et al.[11] reported a value of 0.4 per 1000 monomer units for a polymer produced in concentrated solution (4.6 M) in dichloroethane at 40 °C using azobis(isobutyronitrile) as initiator. Consequently, for the sake of simplicity, the initiator residues will not be considered in the simulations.

As already mentioned, many features of the irregular structures in PVC can be explained from the rearrangement of the radical resulting from the head-to-head addition initially suggested by Rigo.[12] The resulting structures are reported in Scheme II.

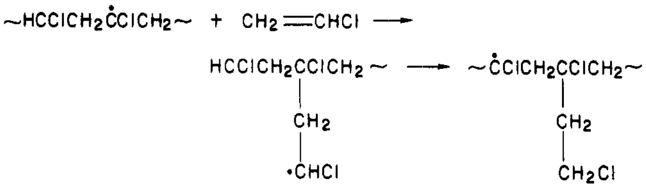
The normal head-to-head structure that might be produced without rearrangement of the radical was not detected in PVC.[3,4] Such a structure could have also been produced by a coupling termination mechanism. This structure and termination mechanism will not be considered further. Among the three possibilities after the 1,2 chlorine migration, the first, which leads to a vinyl chain end (vii) can also be taken as negligible, because it was estimated to be 2% of the total unsaturation.[8] The other two are important: (vi) leads to the formation of a C_1 chloromethyl branch, which is the main branch structure, and (viii) is at the origin of the main unsaturated chain end. In addition, the saturated chain end (ix) produced after reinitiation of the polymerization by the chlorine radical is considered to be the main source of saturated chain ends and is the last step of the actual transfer mechanism that regulates the polymer molecular weight, since it is estimated to be about 1 chain end per polymer chain.

The second main type of mechanism to be considered is transfer to the polymer. Both the regular growing radical and the chlorine radical atom are able to abstract one hydrogen atom from the polymer. For the regular growing radical, the most important reaction is the so-called "back-biting" reaction, which gives rise to a C_4 2,4-dichlorobutyl branch; such branches rank, quantitatively,

Scheme II



second after the C_1 chloromethyl branch. A small concentration of 2-chloroethyl branches were also observed by Starnes[4] and Hjertberg.[13] They also are believed to be formed through a back-biting reaction, mostly at high temperatures. Finally, long branches are formed after random attack on the polymer by the regular growing radicals. It might be noted here that the C_2 branches can be formed if, after transfer onto the polymer and one propagation reaction from the new polymer radical, a second transfer reaction to polymer occurs



$$\sim HCClCH_2\dot{C}ClCH_2\sim + CH_2{=}CHCl \longrightarrow \underset{\substack{|\\ CH_2\\ |\\ \cdot CHCl}}{HCClCH_2CClCH_2}\sim \longrightarrow \sim\underset{\substack{|\\ CH_2\\ |\\ CH_2Cl}}{\dot{C}ClCH_2CClCH_2}\sim$$

Such a mechanism is similar to the double back-biting suggested by Willbourn[14] for polyethylene: it has been recently considered by Starnes et al.[4] for PVC as a double back-biting giving rise to either 2-ethyl-*n*-hexyl or 1,3-diethyl branches. But the corresponding resonances in the ^{13}C NMR spectra of the reduced polymer were not observed.

All these reactions involving the regular growing radical are considered quite selective in that the abstracted hydrogen atom is a tertiary H atom of the –CHCl– group, so that these reactions generate a tertiary chlorine atom considered to be important for the initiation of the dehydrochlorination reaction. On the other hand, the chlorine radical atom is much more active and less selective. If, instead of the reinitiation reaction, it reacts with the polymer, then HCl is produced, and, further, each kind of H atom can be abstracted. From chlorination studies of PVC and its model compounds, it may be inferred that H abstraction on a $-CH_2-$ group will be preferred[15] but not exclusively. If the abstraction is from a –CHCl– group, a long branch will be produced and also a tertiary chlorine atom, as above. But the radical produced after the abstraction from a $-CH_2-$ group is not stable, and a rearrangement is likely to occur, with the formation of an internal double bond and a new chlorine atom. All these mechanisms are reported in Scheme III.

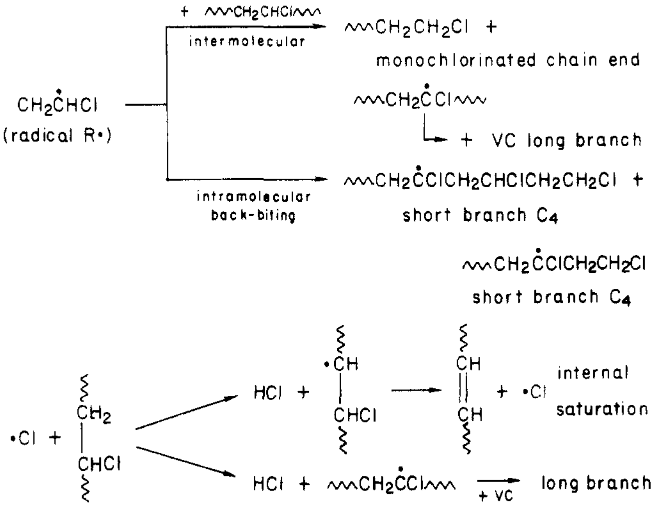
In short, we will consider a kinetic chain without the initiation reaction and also without the termination reaction. This means that we assume that the number of molecules produced between these events is large enough that, from the point of view of defect generation, the

Table I
Analytical Functions for Structural Defects[a]

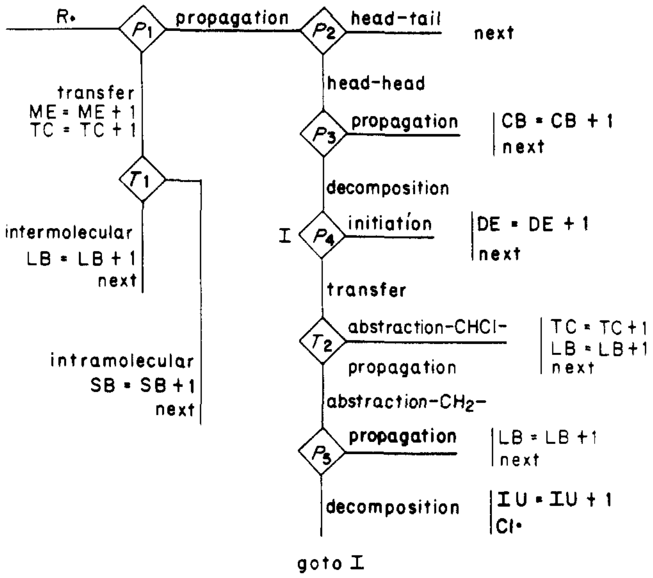
nature of defect		notation	analytical expression
monochlorinated chain end	$-CH_2CHCl$	ME	$1-P_1$
dichlorinated chain end	$-CHClCH_2Cl$	DE	$P_1(1-P_2)(1-P_3)P_4[1/(1-x)]$
unsaturated chain end	$-CH{=}CHCH_2Cl$	UE	$P_1(1-P_2)(1-P_3)$
internal unsaturation	$-CH{=}CH-$	IU	$P_1(1-P_2)(1-P_3)[x/(1-x)]$
chloromethyl branch	$-CH(CH_2Cl)CH_2-$	CB	$P_1(1-P_2)P_3$
short branch (from back-biting)		SB	$(1-P_1)T_1$
long branch		LB	$(1-P_1)(1-T_1)+P_1(1-P_2)(1-P_3)(1-P_4)[T_2+P_5(1-T_2)][1/(1-x)]$
tertiary chlorine	$>CClCH_2-$	TC	$(1-P_1)+P_1(1-P_2)(1-P_3)(1-P_4)T_2[1/(1-x)]$
hydrochloric acid production		HA	$P_1(1-P_2)(1-P_3)(1-P_4)[1/(1-x)]$
number-average molecular weight		M_n	62.5NC/DE

[a] $x = (1-P_4)(1-P_5)(1-T_2)$.

Scheme III
Transfer Mechanisms



Scheme IV
Flow Chart of the Monte Carlo Simulation



number of molecules affected by the initiation and termination reactions is negligible.

The various reactions described in Schemes II and III will be considered in terms of probabilities. The first alternative introduced in the flow chart will be between the propagation and the transfer for a regular chain-end radical (RR). In the case of propagation, the choice will be between a regular head-to-tail and an irregular head-to-head addition. In the first case, a next step of the whole program will be initiated, each step consuming one monomer unit. In the second case, an immediate 1,2 chlorine migration is assumed and the choice is between a rearrangement, which leads to an unsaturated chain end (UE) and a chlorine radical atom, and a propagation, which leaves a chloromethyl branch (CB). For the chlorine radical, the choice will be between a reinitiation step, which produces a new polymer molecule (NM) with a dichlorinated chain end (DE), and a transfer to the polymer.

If transfer to the polymer is to be considered from the regular polymer radical, in each case a saturated monochlorinated chain end (ME) will be produced, as well as a tertiary chlorine atom (TC), and the choice will be between a back-biting intramolecular transfer that produces a short branch (SB), and an intermolecular transfer that will produce a long branch (LB). A possible set of consequent reactions is to consider different probabilities for the butyl branches (BB) and the ethyl branches (EB); this is justified only if samples polymerized at different temperatures are to be compared.

When the chlorine radical atom reacts with the polymer, a molecule of hydrochloric acid (HA) is produced by abstraction from a –CHCl– group, which leaves a tertiary chlorine and will produce a long branch, or by the abstraction from a CH_2 group. In the last case, a new propagation step will leave a long branch without tertiary chlorine, but the most probable event is a rearrangement that produces an internal unsaturation (IU) with regeneration of the chlorine radical.[5]

In Scheme IV, these features of the flow chart of each step in the main loop are illustrated as well as some typical characteristics of the basic program.

Thus, seven probabilities are involved, which may depend on the polymerization conditions (temperature and pressure) as well as on the concentration of the reactants. Before discussing these points, it is necessary to recall some basic features of the vinyl chloride polymerization. The polymerization is mainly a heterogeneous process because the polymer is totally insoluble in its monomer and is precipitated at the very beginning of polymerization in fine particles, their number being fixed at a very low conversion (<1%).[16] However, the precipitated polymer is swollen by the monomer at saturation. It is generally accepted that polymerization takes place mainly inside these swollen particles, because the polymer initiated in the surrounding liquid monomer phase is immediately captured by the existing particles.[17] As long as the liquid monomer phase still exists, the pressure in the reaction is kept constant, and the monomer concentration inside the swollen polymer phase is also kept constant. Under such conditions all the probabilities quoted above are constant.

From these constant probabilities, P_1–P_5 for propagative reactions and T_1–T_2 for transfer reactions, simple analytical expressions can be derived for calculating these defects. They are reported in Table I.

Table I also includes an expression for the number-average molecular weight, which is the ratio between the amount of polymerized monomer and the number of new molecules formed after a chlorine radical has reacted with the monomer. When all the liquid monomer phase has been consumed, the polymer particles cease to be saturated and the monomer concentration inside the particles begins to decrease as the total monomer conversion increases. There is a critical conversion, called the saturation conversion (SC), beyond which some of the above probabilities involving events followed by a propagation step (P_1, P_3, P_4, and P_5) should be corrected.

On the other hand, P_2, which decides between two different propagation reactions, or T_1 and T_2, which compare two kinds of transfer reactions, are not expected to be dependent on monomer concentration. For these probabilities, depending on monomer concentration, a correction factor Y must be introduced. The simplest way is to consider a first-order dependence, so that Y may be written as

$$Y = (1 - K)/(1 - \mathrm{SC}) \qquad (1)$$

where K = SC if the conversion is lower than SC and K = C for higher conversion.

Results and Discussion

The last step of the simulation is to make a correct estimate of the main parameters: the saturation conversion, SC, and the seven probabilities P_1–P_5, T_1, and T_2. Reliable data are available concerning the critical conversion for pressure drop. A typical value is 0.77 for SC at 55 °C;[18] it is expected to decrease if the swelling of the polymer by its monomer increases, i.e., when temperature increases.

P_1 for regular propagation is very high; the total number of short and long branches produced through the transfer mechanism to the polymer from the normal propagating radical is always lower than 1 per 1000 vinyl chloride (VC) units, so that P_1 is higher than 0.99.

P_2 is also high for regular (head-to-tail) propagation; based on the number of C_1 branches plus unsaturated chain ends UE, a reasonable value for P_2 is 0.995. The competition between CB and UE is in favor of propagation; however, the value of P_3 might be estimated as around 0.8. The values for P_4 and P_5 are more difficult to estimate. However, the rather high number of dichloro-saturated chain ends (about 1 per molecule) would give a high value for P_4. We suggest a value of at least 0.8, possibly 0.9. On the other hand, Kolinsky's data[15] for PVC chlorination suggests that the abstraction of an H atom by a Cl· radical takes place preferentially at a CH_2 group. If we assume that the Cl· radical is totally unselective, the value of T_2 would be 0.33. For P_5, it seems that the number of long branches with tertiary H atoms is very limited, so that P_5 is probably low and we suggest a value around 0.1.

Finally, for T_1, the competition is certainly in favor of intramolecular back-biting. A reasonable value would be 0.8–0.9, because the short branches (SB) include all the branches shorter than 5 carbon atoms.

With the above set of probabilities, both analytical calculation and Monte Carlo simulation have been carried out. The results of the analytical calculation are reported in Table II (under SC = 0.72). Comparison with the Monte Carlo calculation gives good agreement provided the number of events (monomer units N) considered in each run is large enough (about 10^6).

In the last three columns of Table II, examples of results for the Monte Carlo calculation are reported. They show that branches (short and long), tertiary chlorine atoms, saturated chain ends, and, to a lesser extent, internal unsaturation generally increase as conversion increases. On the other hand, the number of chloromethyl branches decreases slightly. All these trends are in qualitative agreement with experimental data, but large quantitative differences are observed. The two major discrepancies are related to the relative amount of saturated and unsaturated chain ends and the amount of branches, saturated chain ends, and unsaturation produced under subsaturation conditions (conversion higher than SC).

Table II
Example of Monte Carlo Simulation with Assumed Probabilities $P_1 = 0.9995$, $P_2 = 0.995$, $P_3 = 0.8$, $P_4 = 0.8$, $T_2 = 0.33$, $P_5 = 0.1$, and $T_1 = 0.8$[a]

		conversion			
		SC = 0.77	$C_1 = 0.8$	$C_2 = 0.85$	$C_3 = 0.90$
saturated chain ends	ME × 10^3	0.5	3.0	16.9	41.4
	DE × 10^3	0.91	0.91	0.94	0.96
unsaturation	UE × 10^3	1.0	1.0	1.04	1.08
	IU × 10^4	1.37	1.44	1.69	2.32
branches	CB × 10^3	4.0	3.96	3.86	3.7
	SB × 10^3	0.4	2.38	13.5	33.1
	LB × 10^3	0.19	0.67	3.45	8.37

[a] $Y = (1 - C)/(1 - \mathrm{SC})$.

According to Scheme IV, it is clear that both chlorinated chain ends, DE, and internal unsaturation as well as a part of the long branches are the consequences of chlorine radical formation, associated with the rearrangement mechanism producing the unsaturated chain end UE. Consequently, the number of DE should be lower than UE. Van der Heuvel's data,[6] as well as those obtained in the IUPAC working party,[7] and our own data[8] show that the reverse is true; one must be careful because the number of DE is estimated from ^1H NMR data for the spectral region between 3.8 and 4.0 ppm from Me_4Si and, as we showed,[8] a part of this must be assigned to a part of chloromethyl branches CB. However, it is likely that the correction is not large enough to reverse the relative amounts of DE and UE. There are thus two possibilities: either dichlorinated chain ends may be produced by another mechanism or there is another source for chlorine radicals. A possible way to produce a dichloro chain end is by the readdition of HCl to an unsaturated chain end.

$$\sim CH_2CH{=}CHCH_2Cl + HCl \rightarrow \sim CH_2CH_2CHClCH_2Cl$$

But, first, the amount of available HCl during polymerization is very limited and, second, such a reaction is very improbable. Hence, we do not really believe in this reaction path, which, however, would reduce the UE number and increase the DE number. Another possible route for DE has been suggested by Starnes[19] as a second migration of the radical (v) (Scheme II), resulting in a dichloroethyl branch. However, this event is judged as very improbable, and the corresponding structure has not been identified in the spectra of the products reduced by Bu_3SnD. On the other hand, Starnes[20] has stated that, for polymers prepared in solution under homogeneous conditions, the chloromethyl branch concentration is essentially independent of the monomer concentration. Thus, the transfer process does not involve a kinetically free chlorine atom and so steps (viii) and (ix) in Scheme II are believed to occur in only one step. If this is the case, one should have DE = UE, and another source of Cl· radical is necessary to account for a larger DE value. In addition, the formation of internal unsaturation would need another explanation because, in Scheme IV, $P_4 = 1$ so that neither T_2 nor P_5 would have to be considered.

Concerning the production of chlorine radicals (atoms), we have seen that they result from the decomposition of unstable radicals such as

$$\mathrm{CH_2Cl\dot{C}HCHClCH_2}{\sim} \quad \text{or} \quad {\sim}\mathrm{CHCl\dot{C}HCHCl}{\sim}$$

The second class of radicals is produced after the abstraction of a H atom from a CH_2 group in the chain; a further possibility would be that the abstraction is carried out by a radical different from the Cl· radical. The only available radical is the normal propagating radical. We suggest the possibility that the back-biting reaction might involve not only the –CHCl– group of the fifth and possibly the third carbon atom of the chain, but also CH_2 corresponding to the fourth or sixth carbon atom. The resulting unstable radicals would give Cl· radicals and an internal double bond near the chain ends.

$$\mathrm{CH_2CHClCH_2CHClCH_2CHClCH_2\dot{C}HCl} \rightarrow$$
$$\mathrm{CH_2CHCl\dot{C}HCHClCH_2CHClCH_2CH_2Cl} \rightarrow$$
$$\mathrm{CH_2CHClCH{=}CHCH_2CHClCH_2CH_2Cl} + \cdot\mathrm{Cl}$$

Such double bonds near the chain end will not be estimated by chemical methods such as ozonolysis[21] used to determine internal double bond because their scission would not significantly change the molecular weight. Although the results of ozonolysis are not very clearly stated,[22] there is a significant difference between the estimate of the total number of double bonds from NMR analysis and the sum of unsaturated chain ends and the internal double bond from ozonolysis. Definitely, the NMR value is higher than the highest value obtained by summing up the chain end and internal double bonds from ozonolysis data. The existence of internal double bonds near the chain end might provide a partial explanation of that difference; the other well-known explanation is that these internal double bonds could be polyene sequences rather than isolated double bonds. If we admit the possibility of the above unselective (or less selective) back-biting reaction, the double bond produced after the rearrangement step might give rise upon heating to a polyene sequence. Such a sequence may be developed on both sides, one of these sides is the chain end, and the polyene sequence would be limited to a triene or tetraene. The existence of such trienes and tetraenes has been traced in the UV spectra of some samples by Verdu,[23] typical data, given in the IUPAC report;[7] show that these polyene structures appear in samples prepared at high conversion with final overheating. *Note*: The final overheating has two reasons. In industry, just after the saturation conversion has been reached, an increase in the temperature is often observed due to the so-called gel effect caused by a decrease in the termination rate. In addition, a thermal treatment is often applied under vacuum to decrease the amount of residual monomer in the polymer; one sample was produced by the IUPAC working party to simulate these conditions. Their total amount is limited to about 0.011 polyene sequences per 1000 VC units. Verdu's data[23] about PVC photooxidation lead him to conclude that these short polyene sequences, the most active ones for photoexcitation, are located at the ends of the polymer chains.

As suggested by Starnes,[19] assuming a one-step decomposition and reinitiation from the 1,2 migrated head-to-head radical [(v) in Scheme II], and with the possibility for a less selective transfer mechanism from the regular radical, a new scheme and flow chart (Scheme V) may be built.

In that flow chart for the sake of simplicity, it has been assumed that, after a transfer onto a –CHCl– group, a selective propagation takes place to give a branch, short or long, and that, after a transfer onto a $-CH_2-$ group, a selective decomposition takes place to give internal unsaturation and a chlorine radical (i.e., P_5 in Scheme IV is null). It is also assumed that the selectivity of the transfer from the normal propagating radical is not dependent on the substrate and is the same for the back-biting reaction and an intermolecular transfer. These assumptions, which are of course too sharp, were made because the simulations show that the main results are not very sensitive to the value of the probabilities chosen for the minor competitions involved; on the other hand, the analytical expression should be much more complex. The associated analytical expressions for the amount of defects are reported in Table III.

Scheme V

Improved Flow Chart—Simple Version

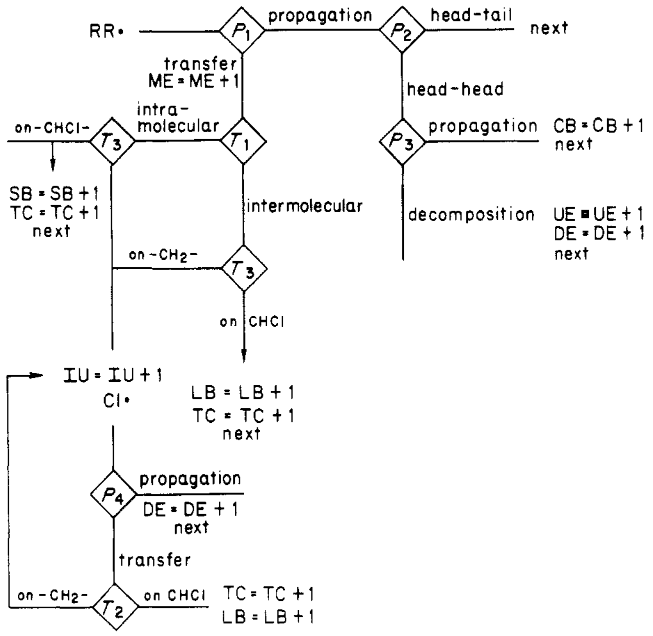


Table III

$\mathrm{ME} = (1 - P_1)$
$\mathrm{UE} = P_1(1 - P_2)(1 - P_3)$
$\mathrm{CB} = P_1(1 - P_2)P_3$
$\mathrm{LB} = \mathrm{ME}[(1 - T_1)T_3 + (1 - P_4)T_2(1 - T_3)(1/(1 - x))]$
$\mathrm{TC} = \mathrm{SB} + \mathrm{LB}$
$\mathrm{DE} = \mathrm{ME}P_4(1 - T_3)[1/(1 - x)] + \mathrm{UE}$
$\mathrm{IU} = \mathrm{ME}(1 - T_3)\ [1/(1 - x)]$
$\mathrm{SB} = (1 - P_1)T_1T_3$
$\mathrm{HA} = \mathrm{IU}$
$x = (1 - P_4)(1 - T_2)$

The best available experimental data[7,8] are for one of the samples of the IUPAC working party: sample XIII polymerized in bulk at 55 °C to 56% conversion, far below the critical SC. Data for that sample are reported in Table IV, together with data from the simulation with Scheme V with one of the best sets of probabilities P_1–P_5 and T_1–T_3. This set has been chosen to give the best fit with data for short and long branches. Each of the experimental values for ME and DE given in brackets includes a part of CB and corresponds to a resonance of the ^{1}H NMR spectra (350 MHz) in the ranges 3.5–3.8 and 3.8–4.0 ppm from Me_4Si, respectively.[8] The agreement seems to be quite good with a slightly too high UE value and an IU value being possibly too small. Actually, the ozonolysis values that show large variation from one laboratory to another do not include the internal unsaturation near the chain end, while the NMR value does. It is interesting to

Table IV

Experimental Data and Simulation (Number of Defect per 1000 VC Units) with Assumed Probabilities $P_1 = 0.9989$, $P_2 = 0.995$, $P_3 = 0.8$, $P_4 = 0.95$, $T_1 = 0.9$, $T_2 = 0.33$, and $T_3 = 0.8$

type of defect	SB	LB	TC	UE	IU	CB	ME + DE + CB	ME	DE
expl value	0.8	0.1	0.9	0.75	0.1–0.3,[a] 0.45[b]	3.8	6.2	(2.7)	(3.5)
simulation	0.79	0.09	0.88	0.99	0.23	4.0	6.3	1.1	1.22

[a] By ozonolysis. [b] From ^{1}H NMR.

Table V

Influence of P_1–P_5 and T_1–T_3 Probabilities of Scheme V on the Amount of Various Defects (Number per 1000 VC Units)

P_1	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.998	0.995	0.995	0.995
P_2	0.995	0.996	0.9985	0.995	0.995	0.9955	0.995	0.995	0.995	0.995	0.995	0.995	0.995	0.995	0.995	0.995
P_3	0.8	0.8	0.8	0.9	0.85	0.85	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.7
P_4	0.95	0.95	0.95	0.95	0.95	0.95	0.8	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
T_1	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
T_2	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.8	0.33	0.33	0.33	0.33	0.33	0.33
T_3	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.7	0.8	0.8	0.8	0.8
SB	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.70	0.79	0.79	0.89	0.69	1.44	3.6	3.6	3.6
LB	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.18	0.09	0.1	0.10	0.08	0.17	0.42	0.42	0.42
UE	0.99	0.8	0.9	0.5	0.75	0.67	0.99	0.99	0.99	0.99	0.99	0.99	1.0	1.0	0.50	1.49
IU	0.23	0.8	0.8	0.8	0.8	0.8	0.25	0.23	0.23	0.22	0.11	0.34	0.41	1.03	1.03	1.03
CB	4.0	3.2	3.6	4.5	4.25	3.82	4.0	4.0	4.0	4.0	4.0	4.0	3.99	3.98	4.48	3.48
ME	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	2.0	5.0	5.0	5.0
DE	1.22	1.02	1.12	0.72	0.97	0.89	1.20	1.22	1.21		1.11	1.32	1.39	1.98	1.96	2.48

note here that the calculated value (from Scheme V with the probabilities given in Table IV) for the double bond located near the chain end and coming from the internal back-biting is 0.18 per 1000 VC units. This value might account for the difference between the IU values from NMR (0.45) and ozonolysis (0.1–0.3). On the other hand, the simulation involves isolated internal double bonds, while the presence of polyene sequences is possible in the polymer. Starnes et al.[24] gave strong evidence for the formation of isolated double bonds when PVC is prepared at low monomer concentration, where the competition between the regular polymerization and various secondary reactions (transfer, decomposition) is in favor of the latter. Upon reduction with Bu_3SnH, through a radical cyclization process, these isolated double bonds form a cyclopentane ring. However, these cyclopentane structures were not detected in the product of reduction of regular PVC at a level of sensitivity corresponding to about 10^{-4} per VC unit, but we are still not sure that the reaction is complete with PVC. Another possibility is that it does not take place when the double bonds belong to polyene sequences. In Table IV the simulated UE value would decrease if P_2 and P_3 were larger. The effect of changing various probabilities is reported in Table V.

The balance between SB and LB is governed by T_1; IU is very sensitive to T_2, CB, DE, and UE, being dependent on P_2 and P_3, but the results are not sensitive to T_2 and P_4 values. This low sensitivity shows that it is not justifiable to introduce a more complex scheme, which might take into account minor events, such as the possibility for the radical produced after a transfer-onto-polymer step to react by transfer as well as by propagation, or the probability P_5 in Scheme IV for a propagation reaction giving a long branch without tertiary chlorine rather than a selective decomposition reaction giving an IU and a chlorine radical. Of special interest is the variation of P_1, which is expected to decrease (as well as P_3) at the end of polymerization or under subsaturation pressure. There is no reliable data available for high conversion at present, because most often the pressure drop is accompanied by an increase in the polymerization temperature; further, the commercial high conversion polymers were often heated under vacuum in order to eliminate the last traces of monomer. In this treatment, extra unsaturation is introduced. However, Hjertberg and Sorvik did publish interesting data[5] for polymerization carried out under pressure lower than saturation pressure P_0. Some of these data are reported in Table VI for subsaturation pressures down to $0.59P_0$.

Table VI

Hjertberg and Sorvik's Data from Subsaturation Experiments[5]

P/P_0	sample	CB	SB	LB	TC	IU
1	C_7	4.0	0.9		0.9	0.25
0.92	A_{10}	4.0	1.6	0.5	2.1	0.42
0.84	A_8	3.7	2.0	1.2	3.2	0.70
	A_9	3.8	0.7	1.2	2.1	0.56
0.75	A_6	3.6	3.0	0.7	0.37	0.54
	A_7	3.8	2.8	1.4	4.2	0.88
0.66	A_3	3.8	2.8	2.0	4.8	0.92
	A_4	3.6	2.2	1.0	3.2	0.64
	A_5	3.6	2.9	1.1	4.0	0.82
0.59	A_1	3.4	3.4	2.0	5.4	0.96
	A_2	3.5	4.0	0.8	4.8	0.78
1	IUPAC XIII	3.8	0.8	0.1	0.9	0.3

Comparisons of the data from TablesV and VI show that the rise in the SB and IU values account for a rather small change in the P_1 value. It may be argued that, due to incomplete reduction of primary halogen,[25] the SB and LB concentrations given by Hjertberg are underestimated by about 20%; however, that correction would not significantly change the value. Unfortunately, the corresponding experimental values for ME and DE are not available. The CB value also varies, which may be accounted for by a small decrease in P_3. It is clear that the correcting factor Y to be applied to the propagation probabilities when the monomer concentration decreases is much lower than the value given by eq 1: the choice between propagation and transfer (P_1) or between propagation and decomposition and reinitiation (P_3) is not exactly proportional to the monomer concentration, and the balance remains well in favor of the propagation in subsaturation pressure conditions. It may be suggested that this is due to restrictions in the mobility of the growing radical, which is attached to a polymer chain strongly associated with the solid polymer.

Conclusions

The Monte Carlo simulation of the generation of structural defects in vinyl chloride polymerization, on the basis of the most commonly accepted mechanisms, leads to rather large discrepancies as compared with the more reliable experimental results reported up to now. At least for samples prepared under carefully controlled conditions and at limited conversions, rather good agreement can be obtained with a simple scheme assuming a lower selectivity for tertiary hydrogen atoms in the process of transfer to the polymer. However, it remains much more difficult to predict quantitatively the behavior of the polymerization process if the conversion is higher than the critical value, when the steady-state conditions cease to be valid, and under subsaturation pressure. Clearly, more detailed data must be obtained before a more sophisticated simulation process can be applied.

Registry No. PVC (homopolymer), 9002-86-2.

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Microenvironment Polarity of Macromolecules in Solution and in the Condensed State. 1. Solvatochromic Approach in Dilute Solution

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ABSTRACT: Quantitative analysis of the microenvironment polarity of macromolecules in dilute solution was performed by the solvatochromic approach: The solvent effects on the transition energies E_T related to the formation of an intramolecular charge-transfer band were compared in a pyridinium dicyanomethylide chromophore $RC_5H_4N^+C^-(CN)_2$, a low molecular weight model analogue ($R = C_2H_5$), and in a probe covalently fixed on seven polymers of various structures, such as poly(methyl methacrylate), poly(dimethylacrylamide), or poly(hydroxyethyl methacrylate). The solvatochromy of both the model and the labeled polymers may be quantitatively analyzed within the framework of Taft's "linear solvation energy relationships": $E_T = E_T^\circ + s\pi^* + a\alpha$, where π^* and α are empirical polarity parameters of the solvent. Dipolar interactions (π^*) always prevail over hydrogen bonding (α), but their respective contributions are not quite identical for the model and the labeled polymers. Comparative analysis of the solvatochromic data allows an estimation of the volume fraction of solvent ϕ_s in the solvation sphere of the probe fixed to the macromolecular chains—$\phi_s = 0.55$–0.78—and of the polymer polarity defined by π^* and α. Because of restrictions of probe orientation, polymers always appear less polar than expected from the chemical structure of their lateral groups.

Introduction

It is well established that for a kinetically controlled reaction of a given reagent with a macromolecular substrate in homogeneous solution a number of factors specific to the macromolecular structure cause a difference between the polymer reactivity (kinetics and selectivity) and that of its low molecular weight model of similar structure.[1,2] Besides intramolecular neighboring-group effects, which have received much attention especially from a theoretical point of view,[3,4] the "effective local solvent medium" in the solvation sphere of the reaction site linked to the polymeric backbone may be easily identified as an important factor:[5,6] with respect to all short-range interactions that may occur in the vicinity of the reaction site, the solvent S, which constitutes the whole solvation sphere for the low molecular weight model, is in competition with the chain backbone and the neighboring groups, which contribute to define the local "microenvironment polarity" through their steric and electronic effects. Within the last decade this concept of local polarity has led to numerous and fruitful studies, but it still remains to be defined in a more quantitative way as are, for instance, solvent effects in organic chemistry.[7] This major goal is not merely of fundamental interest but also of technological importance, since a comprehensive knowledge of polymer reactivity in solution or in the swollen state (cross-linked resins) is a

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