contributions of these two mechanisms cannot be quantified on the basis of the present experiments, the synthesis and use of an antenna polymer system in an aqueous solution have been demonstrated. Since water is a likely component in terrestrial solar devices designed to produce storable fuels, these results have considerable importance in the development of practical solar photochemical processes.

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Registry No. PNMMA (homopolymer), 29320-20-5; 9-(bromomethyl)anthracene, 2417-77-8; (NMMA)·(acrylic acid) (copolymer), 98821-46-6.

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Activation Parameters and Color Effects in the Thermal Dehydrochlorination of Chemically Pretreated Poly(vinyl chloride)

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ABSTRACT: The thermal dehydrochlorination rate of poly(vinyl chloride), measured under nitrogen at temperatures ranging from 170 to 200 °C, has been reduced significantly by chemical pretreatment of the polymer with a mixture of 1-dodecanethiol, di-*n*-butyltin bis(*n*-dodecyl mercaptide), and di-*n*-butyltin dichloride in *o*-dichlorobenzene at 180 °C. Arrhenius plots for the dehydrochlorination, derived from the rates at 0.10% conversion, reveal that the rate reductions caused by pretreatment are associated with decreases of the preexponential factor, A, rather than with increases in the energy of activation. The reductions in A can be related to decreases in the number of thermally labile starting sites for the polyene growth reaction, owing to the deactivation of these structures during the pretreatment process. Activation energies (E's) for pretreated specimens are in the range 21–24 kcal/mol, as compared to a value of 30 kcal/mol for the virgin polymer. These data are shown to be inconsistent with a chain reaction mechanism for which the experimental value of E is equivalent to the energy of activation for the polyene growth reaction (i.e., for chain propagation). However, the E diminutions caused by pretreatment can be related to increased fractional contributions by allylic chlorides to the rate-determining process. At a given extent of dehydrochlorination, reached at a given temperature, the chemically modified polymers are more lightly colored than those that have not been pretreated. This result is ascribed to a decreasing (polyene growth):(polyene shortening) rate ratio with decreasing HCl concentration, and some specific reactions are suggested in order to account for this effect.

In a previous study of the thermal dehydrochlorination of poly(vinyl chloride) (PVC),[1] the reaction was examined in the presence of substances possessing weak carbon–hydrogen bonds, which make highly effective free-radical scavengers. The process carried out in the presence of excess triphenylmethane, found to be the most effective scavenger, was reduced to a constant rate, about 30% of the uninhibited rate at 194 °C. It was argued that determination of the Arrhenius parameters of the so-called maximally inhibited reaction, proposed to be a molecular elimination, would allow the identification of the rate-determining step. Consequently, the latter was identified as the formation of isolated carbon–carbon double bonds along the backbone with the concomitant evolution of

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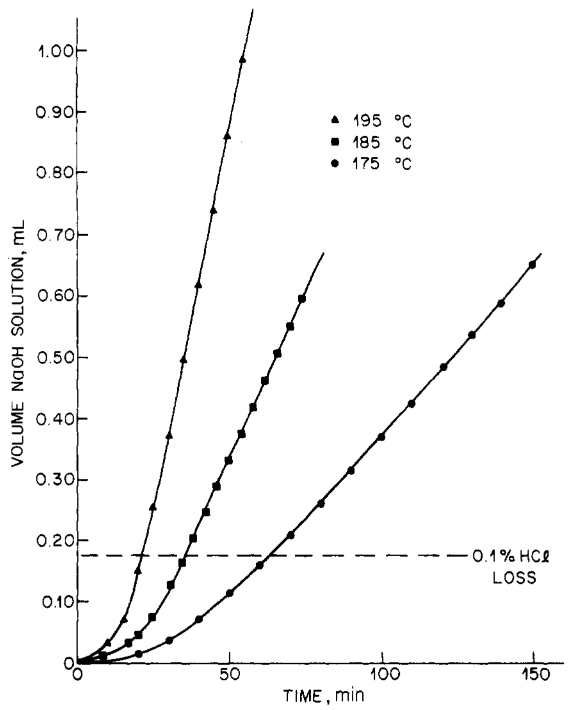


Figure 1. Typical kinetic plots for the thermal dehydrochlorination of virgin PVC under nitrogen at various temperatures.

hydrogen chloride. Under the conditions of maximum inhibition, the free-radical chain component of the reaction was considered to have been eliminated.[2]

Starnes et al. have stabilized PVC by chemically pretreating the virgin resin with organotin compounds[4] and/or thiols[5] in deaerated solutions at 160–190 °C. These workers noted that such pretreatments appreciably reduced the intrinsic reactivity of PVC toward thermal dehydrochlorination, owing to the deactivation, during pretreatment, of thermally labile defect sites.[4,5] While these investigations[4,5] demonstrated that the rate of thermal decomposition diminished at a single temperature, the effects of the given pretreatments on the Arrhenius parameters were not determined. It was felt that, in this respect, the treated resins might behave similarly to maximally inhibited PVC[1] if all of the labile structures in these resins had indeed been removed. Hence the present study was undertaken in order to test that hypothesis, and, as will be seen, it has led to different results.

Results

Experimentally, this study differs from the earlier one[1] in the choice of method for monitoring the progress of the thermal decomposition of PVC. In the earlier study the reaction was carried out to a predetermined conversion level (about 5–10% HCl loss), then terminated by quenching in order to allow the HCl analysis to be performed. Thus each experimental run produced a single result, from which it was impossible to detect an induction period or to observe nonlinearity of data. However, that technique did permit the use of inhibitors mixed with the PVC. Another difference was that the PVC studied previously was in film form, whereas powders were used in the present experiments.

In the present study, monitoring of HCl was conducted by means of an autotitration system (see Experimental Section), which produced continuous data for evolved HCl as a function of time. Such results can be displayed as shown in Figure 1. Each such plot generally had an induction period (which may have been real or may have been due simply to the time lag required for the system to equilibrate thermally), followed by a constantly accelerating HCl production period with no part of the curve being truly linear. Nonlinearity was particularly pronounced for chemically pretreated samples (Figure 2). A useful procedure was developed to overcome deviations from linearity, i.e., measurement of the instantaneous rate at the point of 0.10% HCl loss. At this low level of conversion, cross-linking is likely to have been of little importance.[6] Adoption of this approach overcame the difficulty of dealing with induction periods that varied with decomposition temperature, as well as the problem of dealing with the curvatures of plots, attributable to the autocatalytic nature of the process.

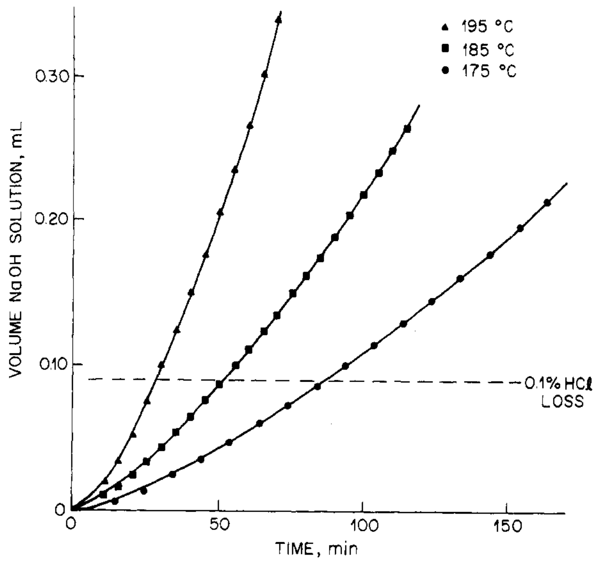


Figure 2. Typical kinetic plots for the thermal dehydrochlorination of chemically pretreated PVC under nitrogen at various temperatures. The pretreatment was carried out for 70 h with a mixture of 1-dodecanethiol, di-*n*-butyltin bis(*n*-dodecyl mercaptide), and di-*n*-butyltin dichloride as the reagent; see Experimental Section for further details.

Rates were measured over the temperature range 170–200 °C for the thermal dehydrochlorination of (a) unstabilized virgin resin, (b) unstabilized virgin resin that had been dissolved in *o*-dichlorobenzene and precipitated by addition of the solution to excess methanol, and (c) resins that had been subjected to chemical pretreatment in *o*-dichlorobenzene and had then been recovered by precipitation in the manner used for b. The pretreatment reagent selected, a mixture of 1-dodecanethiol, di-*n*-butyltin bis(*n*-dodecyl mercaptide), and di-*n*-butyltin dichloride, had already been shown to be capable of significantly improving the thermal stability of the polymer.[5]

Hydrogen chloride evolution was assumed to obey first-order kinetics with respect to "PVC concentration" at the very early stages of the decomposition; hence we could write $d[\mathrm{HCl}]/dt = k_1[\mathrm{PVC}]$. It is clear from this equation that the rate equals the rate coefficient, k_1, when [PVC] = 1. Experimentally, the rates were measured in terms of mol of HCl (0.1 g of PVC)$^{-1}$ min^{-1}. These data were fitted by linear regression analysis to yield Arrhenius plots. The preexponential factors, *A*, were then multiplied by the appropriate factor for conversion into units of mol of HCl (mol of PVC monomer units)$^{-1}$ s^{-1} (or simply s^{-1}, when written in the conventional way).

Figure 3 displays the Arrhenius plots for virgin PVC and for three PVC specimens that had been subjected to chemical pretreatment for different lengths of time (see Experimental Section for details). In general, the experimental points in the figure represent the mean values obtained from at least two runs that gave k_1's agreeing to

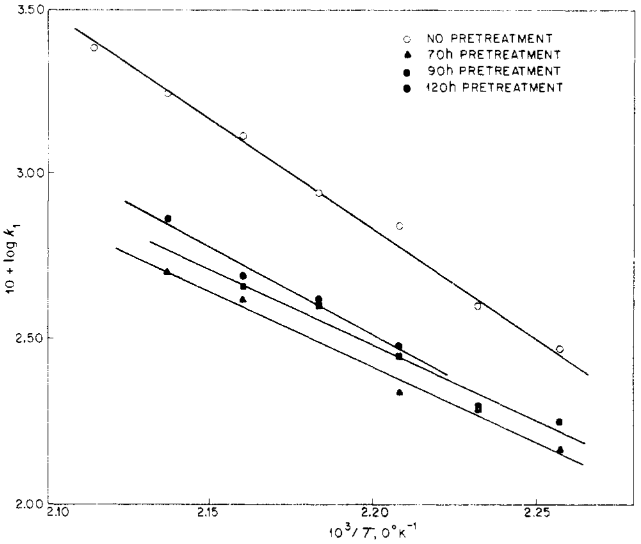


Figure 3. Arrhenius plots for the thermal dehydrochlorination, under nitrogen, of virgin PVC and PVC that had been chemically pretreated with a mixture of 1-dodecanethiol, di-*n*-butyltin bis(*n*-dodecyl mercaptide), and di-*n*-butyltin dichloride. Units of the dehydrochlorination rate constant, k_1, are mol of HCl (0.1 g of PVC)$^{-1}$ min^{-1}; see Experimental Section and Results for more details.

Table I
Arrhenius Activation Parameters for the Nonoxidative Thermal Dehydrochlorination of PVC

pretreatment^a time, h	E,^{b} kcal/mol	log A,^{b} s^{-1}	no. of kinetic runs
0	30.0 ± 0.5	8.3 ± 1.1	45
70	20.6 ± 0.7	3.3 ± 2.3	10
90	21.0 ± 0.6	3.6 ± 1.9	9
120	24.1 ± 0.8	5.1 ± 2.1	8

^{a}For experimental details, see text. ^{b}Values obtained by linear regression analysis; deviations represent the 90% confidence limits.

within ±10%. Since the virgin and precipitated virgin samples gave plots that were identical within the probable limits of error, the data for these two materials have been combined in order to construct the line for the nonpretreated polymer. It is perhaps worth noting that the stabilizing effects of the pretreatments used here are somewhat less than those to be expected on the basis of earlier work.[5] This finding can be attributed to significant differences between the methods used previously[5] and currently for the stability determinations.

Table I contains the Arrhenius parameters deduced from the plots of Figure 3.

Discussion

Stabilization by Chemical Pretreatment. Earlier work has shown that the chemical pretreatment of PVC with 1-dodecanethiol destroys thermally labile defect structures and produces PVC specimens that exhibit enhanced stabilities (lowered rates of thermal dehydrochlorination) in solution as well as in the solid state.[5] Similar observations have been made for PVC samples that had been subjected to prior reaction with mixtures of di-*n*-butyltin bis(*n*-dodecyl mercaptide) and di-*n*-butyltin dichloride.[4,5] In the case of polymers pretreated with the tripartite reagent of the present study, dehydrochlorination rates have been determined only for solid specimens. Nevertheless, in view of the pretreatment results, just described, that are afforded by the components of this reagent, there is certainly no reason to believe that polymers pretreated with it would not also exhibit improved stabilities in the liquid phase. Thus it would seem that the stability enhancements found in the present work could not have depended significantly upon the morphological features of our solid PVC samples.

Purification of our pretreated polymers due to their dissolution and reprecipitation also is unlikely to have contributed to their improved stabilities, since these same operations had no kinetic effects on the virgin resin. Furthermore, elemental analyses (Experimental Section) convincingly rule out the possibility, already unlikely, of significant stability enhancements arising from major structural changes during pretreatment or from the physical occlusion of stabilizers into the pretreated samples. We conclude, therefore, that the stabilization caused by our pretreatment reactions could only have resulted from the chemical deactivation of labile polymer structures whose original concentration was quite low.

Activation Parameters. In theory, our pretreatment reactions might have removed so many labile defects that the dehydrochlorination process would have been initiated mostly by the ordinary monomer units in the earliest reaction stage. The activation energy for this stage should then have been considerably greater than that for the earliest stage of the dehydrochlorination of the untreated resin. In order to investigate this possibility, we first attempted to determine the rates at zero time by computerized fitting of the rate curves to polynomial equations from which these rates were to be extracted. Unfortunately, this approach gave results that were not reproducible. Satisfactory reproducibility was achieved for our rates at 0.10% conversion, but Table I reveals that, in contrast to expectations, these rates correspond to energies of activation that are much less for the pretreated samples than for the untreated resin. Thus, at the level of conversion to which our rates apply, the stability improvements due to pretreatment can be ascribed entirely to decreases in the Arrhenius preexponential factor, *A*.

These decreases can be accounted for, in turn, by reductions in the number of labile structures that served as points of departure for the "zipper" dehydrochlorination of the polymer that generates polyene sequences. However, a statistical change in the rate of initiation is probably not the only source of the variation in *A*. Other factors that may have contributed are (a) a statistical change in the rate at which new initiating structures were created during dehydrochlorination and (b) variation among the polymer specimens with respect to the average number of HCl molecules produced per starting site. The formation of new labile defects (allylic chloride moieties) would have been catalyzed by the liberated HCl,[7] and it will be argued in the following section of this paper that decreases in the concentration of free HCl in the polymer would have led to decreases in the average length of the polyene sequences. The latter decreases could have corresponded to reductions in the average amount of HCl produced per labile starting point. Therefore, insofar as factors a and b are concerned, decreases in the HCl concentration could have tended to decrease *A*. Since the HCl concentration would have been reduced, in turn, by decreases in the rate of initiation, it follows that reductions in the original number of labile structures might have tended to reduce the *A* parameter in a total of three ways. Owing to the likely incursion of factors a and b, the relative magnitudes of our experimental *A* values are not necessarily an exact measure of the relative numbers of labile groups in our undegraded PVC specimens.

Now let us consider the physical significance of the energy of activation. Its interpretation depends, of course, upon the mechanism by which the dehydrochlorination takes place.

One possible type of mechanism involves a slow initiation process that gives a molecule of HCl and is followed by a very rapid "zipper" propagation reaction and a competing unimolecular fast termination that stops the polyene growth. In this mechanism the concentration of growing polyenes remains at a low steady-state level, and when a steady-state kinetic treatment is carried out on the simplest form of the mechanism (which assumes that the reactivities of the growing polyenes toward propagation and termination are independent of polyene length), the experimental rate constant, k_1, is found to be equal to $k_i[1 + (nk_p/k_t)]$, where the subscripts i, p, and t refer to initiation, propagation, and termination, respectively, and n is the average number of HCl molecules formed in the polyene growth reaction (i.e., during chain propagation). If the polyene sequences are lengthy, then $n \gg 1$, $k_p \gg k_t$, and the expression for k_1 reduces to nk_ik_p/k_t. Under these circumstances, the experimental activation energy, E, is given by $E_i + E_p - E_t$ and should be approximated by E_i, since propagation and termination have been assumed to be much faster than initiation, and the activation energies of these two steps should thus be relatively small.

Another mechanistic interpretation, championed recently by Danforth,[7,8] proposes that the growing polyenes, once initiated, live for very long times before their growth (propagation) is stopped. Hence their concentration quickly reaches a level that suffices to make propagation the principal rate-limiting HCl source, and even at very low extents of conversion, the experimental energy of activation is equal to E_p.[8] This hypothesis leads to two predictions concerning the E's of our virgin and pretreated polymers. If E_p were independent of the HCl concentration in a degrading specimen, then E should be the same for all of our PVC samples. Alternatively, if HCl catalysis of propagation were to decrease E_p, then E for the virgin polymer should be less than the other E values, because the more reactive virgin specimen would contain the highest concentration of HCl.

Neither of these predictions is consistent with the E values in Table I. Thus our results seem to provide some evidence against the Danforth mechanism and in favor of a mechanism where E is determined primarily by the value of E_i. If the latter type of mechanism is indeed operative, then it follows from our E data that the initiation sites in the pretreated samples must have differed from those in the virgin polymer with respect to structural type. Structures containing tertiary or allylic chloride are thought to be the principal initiators in virgin PVC,[9] and under the conditions of our pretreatment reactions, most (or all) of these species originally present would have been likely to be destroyed.[10] On the other hand, during pretreatment, the ordinary monomer units might have experienced minor losses of HCl, which could have led to low residual concentrations of allylic chlorides [$-(CH{=}CH)_xCHCl-$, where $x \geqslant 1$] in the pretreated specimens. Hence, the E reductions caused by pretreatment could have been due to increases in the percentage of initiation from allylic chlorides, in general, or from allylic chlorides containing larger numbers of conjugated double bonds.

However, there is another mechanistic possibility that needs to be addressed. According to this interpretation, the growing polyenes do, in fact, live for long times, but at 0.10% conversion, their concentration has not always attained the level that causes the rate contribution from initiation to be insignificant. In the case of the virgin polymer, the time required to reach a given conversion is relatively short. Thus the fraction of initiating sites remaining intact at 0.10% conversion is greater for this polymer than for the pretreated specimens. As a result, at 0.10% conversion, the fractional contribution of initiation to the total rate is relatively large for the virgin material, and the lower E values obtained for the pretreated samples can then be ascribed to increased fractional rate contributions from the allylic chloride moieties that are involved in propagation.

The available data provide no basis for choosing between the scenario just described and the mechanism for which E is approximately equal to E_i. Nevertheless, it is important to note that in both cases, the E reductions due to pretreatment can be related to enhanced contributions by allylic chloride groups.

Other interesting features of our data are that the rates for the pretreated samples increase slightly with increasing pretreatment time and that these rate enhancements are due entirely to increases in A. In line with our previous discussion, these observations imply that pretreatment for more than 70 h caused a gradual increase in the number of labile starting sites.

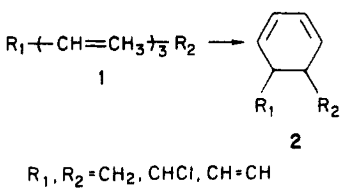
Effects of Dehydrochlorination on Polymer Color. One might have thought that a decrease in the rate of polyene initiation, owing to a reduction in the number of labile starting sites, would have led to an increase in the average length of the polyenes at a given level of dehydrochlorination. Thus one might have predicted that at comparable dehydrochlorination conversions, the polyenes would be longer in our pretreated polymers than in our untreated specimens. Interestingly, however, the converse seems to apply, in that at any given conversion level that was reached at a given temperature, the chemically modified samples were much lighter in color than those that had not been pretreated.[11] Of potential practical significance for the color stabilization of PVC, this intriguing result implies that most of the polyenes in the pretreated resins were too short to absorb visible light. Such an inference is, in fact, supported strongly by the parallel behavior of PVC samples that have been treated with alkylaluminums in order to destroy labile sites.[12] After their thermal dehydrochlorination (which is relatively slow, as expected), such resins also exhibit uncommonly light coloration, and UV analysis shows that the polyene sequences in them are, indeed, unusually short.[12] It is reasonable to believe that the shortening is related in some way to the HCl concentration,[12b] and this hypothesis seems to be confirmed by some results of Hjertberg and Sörvik,[6] who studied the thermal dehydrochlorination of virgin PVC at 190 °C under different partial pressures of HCl and found that the polyene length decreased (at constant conversion) with decreasing HCl pressure when low HCl pressures were used.[13] Up to any given level of dehydrochlorination, the mean concentration of HCl obviously would have been lower in our slowly decomposing pretreated resins than in our less stable virgin polymer. Thus we are led to conclude that our decomposed, pretreated samples exhibited reduced coloration because of low HCl concentrations that led, in turn, to decreases in the rate of polyene elongation relative to the rates of reactions that reduced the polyene sequence length.

In theory, low HCl concentrations could shorten the sequences by reducing the rate of their acid-catalyzed migration along the polymer chain, a process that would lengthen the sequences by bringing them together (eq 1).[14] However, this hypothesis cannot easily account for large

$$-(\mathrm{CH{=}CH})_n-\cdots-(\mathrm{CH{=}CH})_m- \xrightarrow{\mathrm{HCl}} -(\mathrm{CH{=}CH})_{n+m}- \quad (1)$$

color differences at low conversions, where the probability of having more than one sequence per chain is very small.

Two general processes for polyene shortening can be envisaged: (a) intrasequence reactions that convert a sequence into two shorter ones and do not terminate its growth (it may or may not be growing at the time such reactions occur), and (b) reactions that occur at the growing end of a sequence and stop its growth at that point. Both types of reaction could lead to cross-link formation, but different extents of cross-linking are unlikely to have been responsible for our observed differences in polymer color, since at a given conversion and temperature, the extent of cross-linking of all of our samples should have been essentially the same.[6] Therefore, intramolecular shortening reactions (types a and b) are a more likely source of the color phenomena, and from the preceding discussion it follows that these reactions are required to be inhibited (or, at least, not accelerated significantly) by HCl. Attractive candidates for such reactions are cyclizations of triene segments (1) into diene structures (2) (eq 2).[3a]



(2)

These reactions require the presence of a central cis double bond in 1, and they could conceivably be inhibited by the acid, HCl, in several ways that would reduce the number of cis double bonds without causing cross-links to form. Described elsewhere[3a] in detail for the case where the inhibitor is a Lewis acid, these processes would either prevent the formation of cis double bonds or involve their acid-catalyzed isomerization into the more stable trans structure.

Low HCl concentrations might also reduce the (polyene growth):(polyene shortening) rate ratio by decreasing the rate of the "zipper" propagation reaction. It is certainly not unreasonable to expect this reaction to be accelerated by an electrophilic acid catalyst,[3a] and earlier workers have argued for its acceleration by HCl,[6] although to us their experimental evidence seems equally consistent with a decrease in the rate of intramolecular polyene shortening. Detailed information about the structure of the degraded resin, unavailable at this time, obviously would help to establish the relative importance of HCl catalysis of polyene growth and HCl inhibition of polyene shortening, insofar as their effects on polymer color are concerned.

Experimental Section

Materials. The virgin PVC was an unstabilized commercial polymer (Geon 103EP) manufactured by BFGoodrich. Tetrahydrofuran (THF) was treated with disodium benzophenone dianion under nitrogen and then distilled under nitrogen immediately prior to use. All other chemicals were highly purified commercial products requiring no further treatment.

PVC Chemical Pretreatments. The general procedure for these experiments has been described elsewhere in detail.[4a] In the present investigation, all of the pretreatments were carried out under nitrogen at 180 ± 5 °C, using solutions of PVC (3.00 g), 1-dodecanethiol (20.00 g), di-*n*-butyltin bis(*n*-dodecyl mercaptide) (5.90 g), and di-*n*-butyltin dichloride (2.00 g) in *o*-dichlorobenzene (300 mL) (cf. experiment 26 in Table I of ref 5). The resultant polymers were obtained as off-white powders after they had been isolated and purified in the usual way[4a] (precipitation into methanol, followed by Soxhlet extraction with methanol and drying at ca. 50 °C under vacuum). In the case of the pretreatment reactions carried out for 70 or 90 h, the pretreated polymers were prepared in several batches that were combined by dry blending before they were used. Samples pretreated for 120 h were blended by dissolving them together in purified THF under nitrogen, precipitating the polymer into a large excess of methanol, and then drying under vacuum at approximately 50 °C. All of the blends were shown to be homogeneous by replicate rate experiments and duplicate elemental analyses,[15] which gave values that were identical within the probable limits of error. Anal. Calcd for C_2H_3Cl (pure PVC): Cl, 56.73. Found (70-h polymer): Cl, 56.44; S, 0.36; Sn, 0.0014. Found (90-h polymer): Cl, 55.22; S, 0.39; Sn, 0.0061. Found (120-h polymer): Cl, 55.03; S, 0.56; Sn, 0.022.

Kinetics. Thermal decomposition rate studies were performed with an autoburet/pH measurement cell, Model ABU80 (Radiometer, Copenhagen). Powdered PVC samples (0.1000 g) were placed in a Pyrex glass tube and thermostated at the appropriate temperature while a preheated nitrogen stream (30 mL/min) was passed over the decomposing polymer in order to carry the evolved HCl into the pH cell. The volume of standardized alkali solution required to maintain a constant pH was monitored by an automatic recording device as a function of time.

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Evidence of Two Different Crystalline Phases of Isotactic *trans*-1,4-Poly(1,3-pentadiene). An Application of the Rietveld Method

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ABSTRACT: An X-ray analysis has been performed according to the Rietveld whole-fitting method on a bulk-crystallized, annealed sample of isotactic *trans*-1,4-poly(1,3-pentadiene). Calculated spectra have been obtained for different conformers in which the side methyl groups are in a cis or skew arrangement with respect to the adjacent double bonds. Comparison with the observed profile indicates that the skew conformation only gives a good agreement. This conclusion agrees with results already obtained by Neto et al. after a vibrational analysis of the same polymer. A comparison with intensities observed by Bassi et al. on an oriented fiber X-ray diagram shows however several major discrepancies. We deduce therefore the existence of two different crystalline phases that can be respectively observed in the bulk-crystallized polymer and in the sample stretched at a high temperature.

Introduction

Bassi, Allergra, and Scordamaglia investigated the crystal structure of isotactic *trans*-1,4-poly(1,3-pentadiene) (hereafter referred to as ITPP) on the basis of the analysis of X-ray oriented fiber patterns. Their results, reported in ref 1 (hereafter paper I), clearly indicate that the conformation of the polymer chain is such that the side methyl groups are in a cis arrangement with respect to adjacent double bonds (cis model). The alternative skew arrangement (skew model), at least as stable as the former,[2] on the basis of conformational energy calculations, was rejected after many unfruitful trials to obtain an acceptable agreement with the observed intensities.

The conclusions of paper I rely indeed on a semiquantitative evaluation of observed intensities, which might induce some caution about the accuracy of the structural parameters, although the overall validity of the structural model appears to be well established. Later on Neto et al. published three papers[3-5] concerning the vibrational analysis of ITPP both in the single-chain approximation and taking into account packing effects. The results of this investigation indicate a better agreement when the skew model is adopted.

These contradictory indications prompted us to undertake a new approach to the problem, and we decided to analyze X-ray powder diffraction data of ITPP according to the Rietveld whole-fitting method.[6] Of course these experimental data would be less detailed than those of an oriented-fiber X-ray diffraction spectrum and would span a smaller 2θ range, but, on the other hand, they would allow a rigorously quantitative comparison between observed and calculated intensities. Moreover with this experimental technique we had the possibility of low-temperature data recording with a consequent better signal-to-background ratio, particularly at larger 2θ values.

Experimental Section

Sample Preparation and Characterization. *trans*-1,4-Poly(1,3-pentadiene) was prepared by inclusion polymerization of *trans*-1,3-pentadiene in perhydrotriphenylene (PHTP) as described elsewhere.[7] The PHTP–polymer adduct was decomposed by hot extraction in boiling penthane. Inclusion polymerization of diene monomers in PHTP gives rise to a rigorously 1,4-trans enchainment as indicated by NMR data. The ^{13}C NMR (50.9 MHz) spectrum of the polymer shows only five peaks[8] ($\delta(C_1)$ 40.29, $\delta(C_2)$ 126.42, $\delta(C_3)$ 137.23, $\delta(C_4)$ 36.81, and $\delta(C_5)$ 19.94), which were assigned to the 1,4-trans isotactic structure. The ^{13}C NMR spectrum of the polymer after diimine reduction[9] shows a higher steric purity if compared with polymers synthesized in solution.[10] Low-angle X-ray scattering and superheating phenomena revealed the presence of extended chains in the paracrystalline native polymer; in particular the melting point (105 °C) and the heat of melting (116.8 J g^{-1}) are higher than those of the polymer annealed at 82 °C[11] (95 °C and 70.3 J g^{-1}, respectively). A very peculiar feature of this polymer is the extraordinary tendency toward the formation of the paracrystalline modification. In fact not only is a very slow cooling from the melt necessary in order to obtain the crystalline state,[12] but it has also been observed that if a crystalline sample is stretched at room temperature, the orientation process takes place with a simultaneous loss of crystalline order, so that the final state shows an X-ray spectrum that is typical of an oriented paracrystalline phase.[13]

X-ray Diffraction Measurements. For the X-ray diffraction data collection the sample holder was gradually filled by repeated evaporation from a $CHCl_3$ solution. The residual solvent was then

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