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Cationic Copolymers of Isobutylene. 7. Reactivity Ratio Determination by Sequence Distributions Obtained through NMR Analysis

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ABSTRACT: The monomer sequence fractions obtained from the ^1H and ^{13}C NMR spectra of the cationic copolymers of isobutylene (I) with isoprene (IP), *trans*-1,3-pentadiene (tP), and 2,3-dimethylbutadiene (DB) were used for calculating their reactivity ratios. A nonlinear regression analysis utilizing a simplex algorithm and an objective function value permitted the computation of the confidence limits with a defined degree of significance. A comparative test of the first- and second-order Markovian models for the best fit of the experimental data was performed. The reactivity ratios of I–IP copolymer were found to be independent of the degree of conversion, feed composition, and type of catalyst. The values obtained were $r_I = 1.56 \pm 0.19$, $r_{IP} = 0.95 \pm 0.17$; $r_I = 0.59 \pm 0.09$, $r_{tP} = 1.03 \pm 0.19$; and $r_I = 3.20 \pm 1.10$, $r_{DB} = 0.98 \pm 0.53$ (95% confidence limits).

Introduction

In previous papers we studied cationic copolymers of isobutylene (I) with the conjugated diene monomers butadiene (B),[1] isoprene (IP),[2] *trans*-[3] and *cis*-1,3-pentadiene (tP and cP),[4] and 2,3-dimethylbutadiene (DB).[5] This study, which was particularly focused on the structural characterization of the copolymers and their monomer sequence distributions, was carried out mainly by ^{13}C NMR spectroscopy. The structural units present in the copolymers were identified and quantitatively determined by assignment of the signals attributable to the monomer sequences, sometimes up to the level of heptads and octads.[6] Using this structural information, it is possible to determine the reactivity ratios of the monomers by means of a method already applied in the study of epi-sulfide copolymers[7], which is based on a computation program proposed originally by Harwood.[8,9] Recently, this approach has found other applications,[10,11] but the starting point may be considered to be the same, i.e., the association of the relationships of copolymerization statistics with the powerful ability of NMR spectroscopy in polymer characterization for testing mechanistic proposals.[12]

We show in the present paper the results obtained by applying this method in determining the reactivity ratios of I when it is copolymerized with IP, tP, and DB. The collected values are compared with the data reported in the literature and, in some cases, the influence of the experimental conditions (e.g., degree of conversion, feed composition, and type of catalyst) is investigated. Also, the correlation of the experimental data with a first-order or a second-order Markovian model by a simplex algorithm is checked.

The systems I–B and I–cP are not discussed because of their greater complexity and the presence in their spectra of more than one structural diene unit in relatively high concentration.[1,4] The present method has recently been applied to the study of the copolymerization of I with the different isomers of 2,4-hexadiene[13] and 1,1,4,4-tetramethyl-1,3-butadiene.[14]

Experimental Section

Materials. I–IP copolymers were prepared by using, as described previously,[2] a mixture of *n*-pentane/CH_2Cl_2 (1:1 by volume) as solvent at −70 °C and $EtAlCl_2$ as catalyst. Table I shows data for the feed composition, conversion, copolymer composition, and sequence fractions (up to the level of pentads) of ten samples used for studying the reactivity ratios of I and IP. Other samples were obtained under the same conditions but with a solution of $AlCl_3$ in C_2H_5Cl as catalyst. Samples of I–tP and I–DB copolymers employed in these investigations were prepared as described previously.[3,5]

Analyses. ^1H and ^{13}C NMR spectra were obtained and analyzed as reported elsewhere.[1,2] The calculation of the reactivity ratios and their confidence interval was carried out by means of an IBM computer with a program (HAMOCO) written in Fortran language.

Results and Discussion

1. Calculation of the Reactivity Ratios from the Sequence Fractions. The method used in the present paper was described in part previously.[7] The original version[8,9] of the computation program used by us as the basis for our method of calculating the reactivity ratios permits one to obtain (i) the copolymer composition, (ii) the dyad, triad, tetrad, and pentad fractions, and (iii) the sequence number and weight distributions, when the feed composition, conversion, and reactivity ratios are known. The computational procedure can take into account the general form of the first-order Markovian model (terminal

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Table I
Sequence Fractions in Isobutylene-Isoprene Copolymers

	sample no.									
	1	2	3	4	5	6	7	8	9	10
feed, mol % of A[a]	83.3	65.0	61.0	55.5	50.0	45.5	83.3	65.0	61.0	50.0
conv, %	2.3	8.2	5.5	7.0	6.6	8.0	32.5	39.6	38.5	40.0
comp, mol % of A										
by ^{1}H NMR[b]	89.2	66.2	68.1	62.0	57.5	54.8	85.2	66.2	65.2	58.3
by ^{13}C NMR	89.8	69.1	69.5	63.7	57.8	53.7	83.3	67.3	69.2	56.6
AAA	0.795	0.513	0.536	0.450	0.391	0.349	0.780	0.474	0.507	0.359
AAB + BAA	0.191	0.389	0.372	0.434	0.448	0.456	0.201	0.412	0.383	0.453
BAB	0.014	0.098	0.092	0.116	0.161	0.195	0.019	0.114	0.110	0.188
BBB	0.026	0.140	0.142	0.171	0.218	0.247	0.075	0.142	0.133	0.239
BBA + ABB	0.292	0.479	0.468	0.489	0.506	0.508	0.283	0.501	0.470	0.474
ABA	0.682	0.381	0.390	0.340	0.276	0.245	0.642	0.357	0.397	0.287
AAAA	0.643	0.259	0.255	0.192	0.119	0.110	0.608	0.225	0.231	0.132
AAAB + BAAA	0.166	0.200	0.206	0.180	0.166	0.074	0.164	0.194	0.218	0.136
BAAB	0.004	0.037	0.039	0.050	0.062	0.058	0.006	0.051	0.044	0.064
AABA + AABB + ABAA + BBAA	0.131	0.242	0.247	0.250	0.233	0.205	0.162	0.249	0.248	0.235
ABBA + BBBA + ABBB + BBBB	0.019	0.113	0.111	0.148	0.192	0.242	0.032	0.124	0.109	0.199
BABA + BABB + ABAB + BBAB	0.035	0.149	0.142	0.180	0.228	0.237	0.028	0.157	0.150	0.234
AAAAA	0.578	0.254	0.254	0.199	0.138	0.116	0.636	0.211	0.242	0.149
BAAAA + AAAAB	0.182	0.229	0.220	0.197	0.186	0.176	0.175	0.220	0.219	0.179
BAAAB	0.020	0.045	0.053	0.064	0.058	0.065	0.020	0.059	0.057	0.047
AAABA + AAABB + ABAAA + BBAAA	0.169	0.267	0.279	0.251	0.267	0.255	0.136	0.278	0.267	0.272
BAABA + BAABB + ABAAB + BBAAB	0.037	0.130	0.115	0.167	0.183	0.204	0.019	0.139	0.130	0.186
ABABA + BBABA + ABABB + BBABB	0.014	0.075	0.079	0.122	0.168	0.184	0.014	0.093	0.085	0.167

[a] A = isobutylene, B = isoprene. [b] The ^{1}H NMR values were used for the evaluation of the reactivity ratios.

reaction scheme) or the second-order Markovian model (penultimate reaction scheme) and the composition of the copolymers obtained at low or high degree of conversion. In fact, the composition and the sequence distributions of instantaneous copolymers are calculated by means of well-known standard relationships.[15] Conversely, when the copolymer is obtained at high conversion, an iterative procedure within the computer program takes into account the effect of the subsequent increments of conversion on the copolymer composition.

A more recent version of the computation program summarized here has been extended to the case of terpolymers,[16] and the importance of the nonlinear analysis for obtaining the best evaluation of the reactivity ratios is becoming widely acknowledged.[17-20] We have employed Harwood's program during our work as a subroutine for an optimizing process that used the feed and conversion data and the values of the reactivity ratios that minimize the root-mean-square difference between the experimental and calculated values of the sequence fractions obtained by NMR spectra. The analysis being nonlinear, an efficient minimizing algorithm, displaying reasonably fast convergence, was found in the simplex method.[21] This algorithm, used for carrying out the nonlinear analysis, was found to be valid, as convergence toward the same pair of values occurred even in the case of largely different initial values. The only constraint introduced in our computation was the use of positive values of r_1 and r_2 and also of r_1' and r_2' in the case of the second-order Markovian model.

The statistical treatment of the experimental data was mainly aimed at providing the best fit of the experimental data according to the first-order or the second-order Markovian model pertaining to the monomer pair considered. However, the use of a higher order model has to be justified by objective statistical tests, as, for instance, the variance ratio test of the square objective function $S(\theta)$[24] (see Appendix), which provides an adequate assessment of the accuracy of the copolymerization model adopted.

Having determined the value of the objective function and the confidence limits as described in the Appendix, before concluding our evaluation we must (i) choose the copolymerization model by computing the pair and the two pairs of parameters pertaining to the first-order and second-order Markovian model, respectively, and (ii) evaluate the possible significance of the difference existing between the values of the reactivity ratios obtained from two different series of samples prepared under different experimental conditions. When overlapping of the confidence limits occurs, the difference of the values of $S(\hat{\theta})$ is considered to be meaningless.[24] The first-order Markovian model is considered more suitable than the second-order model for fitting the experimental results when the decrease of the values of $S(\hat{\theta})$ does not significantly lower the value of the variance (eq A2), which is influenced by the magnitude p of the parametric vector.[24] We observed in the present work that the use of four parameters implies a broadening of the confidence limits and hence a poorer performance of the model, as the gain in the sum of the squared differences does not compensate for the enlargement of the confidence limits.

2. I–IP Copolymer. In a previous paper[2] the NMR spectra and the attribution of signals to different monomer sequences of I–IP copolymer were discussed. The interpretation of the spectra allowed us to calculate the fractions of triads centered both on I and IP and the tetrad distribution. Table I shows also the fractions of pentads centered on I and obtained from 10 copolymer samples

Table II
Copolymerization of I-IP in the Presence of $AlCl_3$ as Catalyst[a]

$AlCl_3$, mmol/L	feed, mol fract of I	conv, %	comp,[b] mol fract of I
1.3	0.83	9	0.89
1.6	0.65	5	0.73
2.0	0.50	5	0.59

[a] Experimental conditions: solvent = *n*-pentane + CH_2Cl_2 (1/1 (v/v)); [I] + [IP] = 3.3 mol/L; $T = -70$ °C; time = 15 min; $AlCl_3$ as a solution in EtCl (0.2 M).
[b] Determined by ^1H NMR.

prepared by varying the feed composition and the degree of conversion.

When all the data collected in Table I are used, the computation method described in the previous section yields (first-order Markovian model) $r_I = 1.56 \pm 0.19$ and $r_{IP} = 0.95 \pm 0.17$, while the value of the objective function is $F_N = 0.137$ (confidence limits with a level of probability = 95%). According to the second-order Markovian model, the values of the corresponding parameters are $r_I = 1.63 \pm 0.28$, $r_{IP} = 0.85 \pm 0.40$, $r_I' = 1.30 \pm 0.47$, $r_{IP}' = 0.97 \pm 0.27$, $F_N = 0.113$, and $\Delta F_N = 0.024$ over two degrees of freedom. The corresponding variance ratio has a value of $0.012/(0.113/14) = 1.5$, which is not significant. It is evident that the use of the second model gives rise to very little reduction of the value of F_N whereas the confidence limits are increased. Therefore, the penultimate reaction scheme has been rejected. The experimental data are correctly described by the two-parameter model, which yields values of r_I and r_{IP} within the confidence limits obtained for r_I and r_I' and for r_{IP} and r_{IP}'.

The data in Table I were then divided into two groups, including samples obtained at high and low conversion (>10% and <10%), respectively, in order to check the validity of the fundamental assumption of the adopted method. The four samples obtained at high conversion yielded $r_I = 1.49 \pm 0.22$ and $r_{IP} = 0.98 \pm 0.20$, while for the other samples obtained at low conversion we have calculated $r_I = 1.56 \pm 0.17$ and $r_{IP} = 0.94 \pm 0.15$, which confirms the agreement of the results obtained in the two cases.

A cationic catalyst different from that reported in Table I was used for synthesizing other samples of I-IP (Table II) in order to check the influence of the type of catalyst on the reactivity ratios. The results obtained, i.e., $r_I = 1.44 \pm 0.26$ and $r_{IP} = 1.03 \pm 0.27$, are very close to the previous ones.

The data reported in the literature for the I-IP system are summarized in Table III. They exhibit some discrepancy when compared with ours, in particular, for the older values of r_{IP}, which are consistently lower than ours. Three hypotheses may be proposed to explain the difference observed: (i) dependence of the values of the reactivity ratios on the feed composition, in particular, when the amount of IP is low; (ii) dependence on the method used for their computation; (iii) dependence on the analytical method used for determining the copolymer composition.

With respect to the first hypothesis, it must be pointed out that the literature data are concerned only with copolymer samples containing a low level of IP, while the method adopted by us requires a higher amount of the less abundant comonomer in order to quantify reliably the signals of the copolymer spectra. However, in order to check point i, we have taken into account the two samples of Table I with lower diene content (IP = 10% and 15%, respectively). The values obtained, $r_I = 1.64 \pm 0.18$ and $r_{IP} = 1.11 \pm 0.18$, are very close to those obtained by considering samples with high IP content. Therefore, the reactivity ratios values do not depend on the copolymer composition within the range examined.

The second hypothesis can be ruled out by using the data of Table I concerning the low-conversion samples in the Fineman and Ross linear computation. The results are $r_I = 1.69$ and $r_{IP} = 1.13$, i.e., very close to the values obtained with a nonlinear computation.

The third hypothesis appears likely, because the older data of the literature were obtained by determining the diene content of the copolymer by iodometric titration,[25] which appears less reliable than NMR spectroscopy owing to the occurrence of substitution side reactions.[26] For instance, the iodometric method did not allow Kennedy to obtain a quantitative balance between the amount of IP introduced in the feed and that found in the copolymer plus the amount of unreacted IP at the end of the copolymerization.[27] If we take into consideration possible cyclization reactions,[28] the content of IP in the copolymer detectable by NMR will be reduced. Therefore, the method we used does not overestimate IP.

In conclusion, we believe that our data are more reliable than those found in the older literature and concerning I-IP samples having a low content of diene. In fact, when the content of IP increases and is determined indirectly by VPC,[34] the resulting values of r_I and r_{IP} (obtained perhaps by a linear regression analysis) are closer to ours than the older values (see Table III). However, it must be pointed out that the samples investigated by us were obtained at higher temperature (−70 °C) and in a solvent different from those used by other authors (see Table III), even though the influence of these differences is expected to be weak.[29]

3. I-tP Copolymer. The computation procedure described in sec. 1 was used also for determining the reactivity ratios of the I-tP system. The sequence fraction values pertaining to two copolymer samples and reported in a previous paper[3] were utilized. The data available extended to the level of hexads, but for our computer program only the fractions up to the level of pentads have been used. The results obtained are (95% confidence limits) $r_I = 0.59 \pm 0.09$ and $r_{tP} = 1.03 \pm 0.19$. The large

Table III
Values of the Reactivity Ratios Reported in the Literature for the I-IP System

		exptl conditions			
r_I	r_{IP}	solvent	catalyst	T, °C	ref
2.5 ± 0.5[a]	0.4 ± 0.1	MeCl	$AlCl_3$	−103	30
2.17[a]	0.50	MeCl	$EtAlCl_2$	−100	29
2.26[a]	0.38	EtCl	$AlCl_3$	−95	31
2.27[a]	0.44	EtCl	$EtAlCl_2$	−90	31
1.75[b]	1.02	MeCl/(C_6 + C_7)[c]	$EtAlCl_2$	−80	34

[a] Copolymer composition determined by iodometric titration.[25] [b] Copolymer composition determined by VPC analysis of unreacted monomer. [c] C_6 + C_7 = hexane-heptane mixture; 50% MeCl.

number of sequence fractions, although obtained from only two samples, permits narrow confidence limits. The use of the second-order Markovian model in the treatment of our data did not allow us to obtain an improvement in the values of r_I and r_{tP}.

4. I–DB Copolymers. The values of the sequence fractions of this copolymer were reported previously.[5] Two samples have been used for the calculation of the reactivity ratios, and the fractions taken into account were only up to the level of tetrads so that the confidence limits (95%) are rather broad. The following values were obtained: $r_I = 3.20 \pm 1.10$ and $r_{DB} = 0.98 \pm 0.53$. The two-parameter model was also found in this case to be more valid than the higher order model.

Conclusions

The method employed in this paper belongs to the group of approaches used for calculating reactivity ratios which utilize the values of the monomer sequence fractions (see, for instance, ref 10, 11, 20, 32, and 33), usually obtained by ^{13}C NMR spectroscopy. The use of copolymer microstructural data allows a significant improvement, from both a qualitative and quantitative point of view, of the methods more widely used in the past for evaluating the reactivity ratios, since they were based only on compositional data. In fact, the study of the monomer distribution in a copolymer furnishes sequence fractions whose values enter the copolymerization relationships as data much more abundant and self-consistent than the simple overall comonomer composition. This is because the sequence fraction values, which are usually a set of independent data for each copolymer sample, imply the attenuation of possible errors involved in the evaluation of the composition (expressed usually by one or a few data for each sample), so that the final result is particularly reliable. Furthermore, the method allows a choice between the first-order and the second-order Markovian model, depending on the best fit of the experimental data, provided that the conditions, pointed out previously by Bovey,[12] for the level of information necessary for testing different copolymerization models hold. More particularly, the approach described here permits computation of the values of the reactivity ratios and their confidence limits by means of a nonlinear regression analysis that utilizes the copolymer composition and the monomer sequence distribution at a defined, but not restricted, monomer conversion. Furthermore, all the data of the sequence fractions, available from the experimental techniques adopted, can be used, but a complete set of values is not necessary. Obviously, more complete sequence fractions permit narrower confidence limits and decrease the number of samples to be examined.

For the three cationic copolymers examined in this work, the most valid model is that described by two parameters (first-order Markovian), and hence an influence of the penultimate units on the reactivity of the active centers can be ruled out. The reactivity ratios of the I–IP pair, studied in more detail, have been found to be independent of such experimental parameters as the conversion, feed composition, and type of catalyst.

The values of the reactivity ratios calculated for the three copolymers synthesized under the same conditions in the presence of $EtAlCl_2$ as catalyst are (within 95% confidence limits) $r_I = 1.56 \pm 0.19$, $r_{IP} = 0.95 \pm 0.17$; $r_I = 0.59 \pm 0.09$, $r_{tP} = 1.03 \pm 0.19$; and $r_I = 3.20 \pm 1.10$, $r_{DB} = 0.98 \pm 0.53$. A comparison with literature data is possible only for the I–IP pair: the reactivity of IP appears higher than that reported by the majority of other authors. The disagreement appears mainly to be attributable to the different methods used for the copolymer analysis and perhaps to the different experimental conditions adopted for the copolymer synthesis.

The method described above requires that each monomer enter the copolymer chain as a unique structural unit. This condition is not rigorously satisfied in the case of diene monomers, because sometimes (e.g., I–tP) small amounts of structures other than the dominant trans-1,4 unit are present. Despite this structural complexity, the abundance of experimental data and the completeness of the set of sequence fractions obtainable from the ^{13}C NMR spectra of some isobutylene–diene copolymers have allowed us to use the method described in this paper successfully.

Appendix

We consider first, for the best estimate of the parametric vector θ, the estimate of the least-squares $\hat{\theta}$ obtained by minimizing a square objective function $S(\hat{\theta})$. When the value of the $\hat{\theta}$ vector that satisfies the condition of the minimum for the function $S(\theta)$ is determined, the approximate confidence limits can $S(\hat{\theta})$. represented by

$$S(\theta) - S(\hat{\theta}) \leq ps^2F_\alpha(p,\nu) \qquad \text{(A1)}$$

where s^2 is an independent estimate of the residual variance with ν degrees of freedom, p is the dimension of the parametric vector θ, and $F_\alpha(p,\nu)$ is the lowest value having probability α (95%) of the F variable with p and ν degrees of freedom. The estimate of the variance (s^2) can be obtained as a first approximation by using

$$s^2 = \frac{S(\hat{\theta})}{n-p} = \frac{S(\hat{\theta})}{\nu} \qquad \text{(A2)}$$

where n is the number of experimental points. By assuming a moderate degree of nonlinearity for the model,[22] a Taylor series developed up to the second order can be adequate for $S(\theta)$. Correspondingly, the confidence limits can be approximated by[23]

$$\frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p}\left[\frac{\delta^2 S(\theta)}{\delta\theta_i\delta\theta_j}\right]_{\theta=\hat{\theta}}(\theta_i-\hat{\theta}_i)(\theta_j-\hat{\theta}_j) \leq ps^2F_\alpha\ (p,\nu) \qquad \text{(A3)}$$

and assuming that eq A4 is verified in the point of optimum.

$$\left[\frac{\delta S(\theta)}{\delta\theta_i}\right]_{\theta=\hat{\theta}} = 0 \qquad \text{(A4)}$$

By using vector notation, eq A3 can be rewritten as

$$(\theta-\hat{\theta})^{\mathrm{T}}v(\theta-\hat{\theta}) \leq ps^2F_\alpha(p,\nu) \qquad \text{(A5)}$$

$2V$ being the $p \times p$ matrix of the second derivatives

$$S^{(ij)} = \left[\frac{\delta^2 S(\theta)}{\delta\theta_i\delta\theta_j}\right]_{\theta=\hat{\theta}} \qquad i, j = 1, 2, ..., p \qquad \text{(A6)}$$

When the first derivative is not rigorously zero, eq A5 will include in the left-hand term also the expression

$$(\theta-\hat{\theta})^{\mathrm{T}}\left(\frac{\delta S(\theta)}{\delta(\theta_i)}\right)_{\theta=\hat{\theta}} \qquad \text{(A7)}$$

Actually, in our case, the two values of the confidence limits were not rigorously coincident. The difference being small, we have computed the average value ($\bar{M}$), and the results are reported as $r_i = \bar{M} \pm A$.

Registry No. Isobutylene, 115-11-7; isoprene, 78-79-5; *trans*-1,3-pentadiene, 2004-70-8; 2,3-dimethylbutadiene, 513-81-5.

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Photochemistry of Ketone Polymers. 17. Photodegradation of an Amorphous Ethylene–Propylene Copolymer

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ABSTRACT: Samples of an amorphous ethylene–propylene (78:22 mol %) copolymer were thermally oxidized to produce polymers with varying amounts of keto and hydroperoxy groups. Additional samples were prepared in which the hydroperoxy groups were removed by thermal decomposition under vacuum. Studies were then made of the quantum yields of chain scission (Φ_s), carbonyl loss (Φ_{-CO}), and terminal vinyl formation (Φ_{II}) in solution and in solid films. Samples containing both carbonyl and hydroperoxide showed much higher values of Φ_s (0.2–1.3) than those containing only ketones ($\Phi_s = 0.036$). Furthermore the results could not be explained by direct absorption of light by the hydroperoxide groups, since in all cases more than 87% of the light was absorbed by the ketone structures. The results are consistent with a relatively efficient transfer of excitation energy from the keto group to hydroperoxide, possibly by the exciplex mechanism recently proposed by Ng and Guillet. At 250 and 276 nm, where strong primary absorption by hydroperoxide occurs, a dark scission reaction was observed, which is attributed to the bimolecular reaction of two peroxy radicals on the polymer chain followed by β scission of the resulting macroalkoxy radical. The significance of these results to the mechanism of polyolefin photooxidation is discussed.

Many studies of the oxidative degradation of polyolefinic materials by ultraviolet or visible light[1-8] or heat[9-13] have been published during the past decade. It has been recognized that the basic reactions in the photooxidation of polyolefins are similar to those occurring in thermal oxidation. The two chemical species believed to be important in causing the thermal degradation and photodegradation of polyolefins are hydroperoxide groups and ketone or aldehyde carbonyls. There has been some controversy in the literature as to whether the hydroperoxide groups or the ketone groups are more effective sensitizers in photooxidation and in maintaining the oxidative chain reactions that lead to polymer degradation.[14-17]

Hydroperoxides are produced in aliphatic or aromatic polymers from polymer radicals formed mechanically or chemically. In the presence of air, these radicals react to give peroxy radicals that are stabilized by hydrogen atom abstraction to give hydroperoxy groups. In cases where the polymer contains relatively large concentrations of double bonds, such as in polyisoprene or polybutadiene, hydroperoxides can also occur by addition of singlet oxygen to form an allylic hydroperoxide,[5,15] although it is unlikely that this reaction is important in the oxidation of saturated aliphatic or aromatic polymers.

Guillet has pointed out that after the initial stages of photooxidation, the accumulation of carbonyl groups will cause the light excitation to be overwhelmingly concentrated on the carbonyl chromophores.[17] Chain scission would then occur via the Norrish type I and II reactions characteristic of ketone compounds as well as those involved in the oxidation process per se. It is, therefore, important to understand the photodegradation of ketone polymers in the presence of hydroperoxide groups on the polymer backbone. It is well established that photooxidation of polyolefins takes place primarily in the amorphous phase. Copolymers of ethylene and propylene

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