

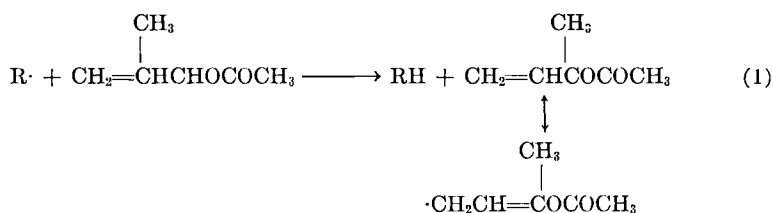
Allyl Polymerization. V. Effective Chain Transfer in the Polymerization of 3-Buten-2-yl Acetate. Polymerization of 3-Buten-2-ol

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INTRODUCTION

In addition to degradative chain transfer,^{1,2} the polymerization of allylic monomers is characterized by effective chain transfer.^{3,4} The structural feature in an allyl compound which participates in these transfer reactions is the α -methylene group which possesses an abstractable hydrogen. A further position which is susceptible to attack in an allylic ester is the methylene group alpha to the carbonyl group in the acid-derived portion of the ester.¹ The present investigation was undertaken in order to determine the effect of the substitution of a methyl group on the carbon atom alpha to the double bond, i.e., in an α -methylallyl ester.

An α -methyl group in an allylic compound results in an allylic position which should be more prone to attack than the unsubstituted allylic compound, since the radical formed by abstraction of hydrogen, i.e., the resultant tertiary radical, is more stable. Therefore, reaction (1) should occur more readily with α -methylallyl compounds than the analogous reaction with allyl compounds and should be reflected in even lower molecular weights.



POLYMERIZATION OF 3-BUTEN-2-YL ACETATE

Results

The bulk polymerization of the acetate of 3-buten-2-ol (α -methylallyl acetate) was investigated using benzoyl peroxide as the catalyst at 80 \pm

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0.1°C. The decomposition of peroxide and the disappearance of monomer were followed as a function of time.

The disappearance of monomer in the polymerization of allyl esters was followed by titrating residual unsaturation in the polymerizing mixture.^{1,2} The unsaturation was presumed to correspond to unreacted monomer. The low DP anticipated in the α -methylallyl series indicated that this method would not be satisfactory since abstraction of hydrogen from the allylic position and subsequent reactions should yield products containing residual unsaturation. By titration this unsaturation would be erroneously calculated as monomer and represent a large error due to the low molecular weight of the polymer. Therefore, in addition to titration for unsaturation, the disappearance of monomer was followed by isolation of nonvolatile material.

Decomposition of Benzoyl Peroxide

The data on the decomposition of peroxide in polymerizing 3-buten-2-yl acetate at 80°C., with approximately 2, 5, and 10% initial catalyst concentration are summarized in Table I and plotted in Figure 1.

TABLE I
Decomposition of Benzoyl Peroxide in 3-Buten-2-yl Acetate at $80 \pm 0.1^\circ\text{C}$.

Initial Bz_2O_2 concn.		% Decomposition			
Wt.-%	Moles/Kg.	0.5 hr.	1.0 hr.	2.5 hr.	5.0 hr.
2.12	0.0876	9.2	19.0	38.9	62.6
5.09	0.2110	12.0	23.0	47.4	71.8
9.86	0.4080	14.7	26.8	53.6	78.3

The decomposition of peroxide is approximately first order, the rate increasing with increased initial peroxide concentration, analogous to the

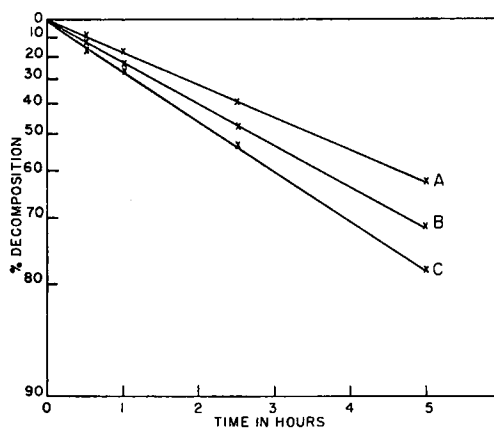


Fig. 1. Decomposition of benzoyl peroxide in polymerizing 3-buten-2-yl acetate at 80°C.: A, 2.12% Bz_2O_2 ; B, 5.09% Bz_2O_2 ; C, 9.86% Bz_2O_2 .

situation with the allyl esters. A comparison of the rate constants for the decomposition of benzoyl peroxide in polymerizing allyl acetate and α -methylallyl acetate indicates a greater induced decomposition in the latter case (see Table II).

TABLE II
Decomposition of Benzoyl Peroxide at $80 \pm 0.1^\circ\text{C}$.

Allyl acetate		α -Methylallyl acetate	
Initial wt. % Bz_2O_2	k_1 hr.^{-1}	Initial wt. % Bz_2O_2	k_1 hr.^{-1}
2.05	0.193	2.12	0.197
4.94	0.223	5.09	0.252
9.96	0.258	9.86	0.305

Rate of Polymerization

The disappearance of monomer, as determined by titration as well as evacuation, is summarized in Table III.

TABLE III
Rate of Polymerization of 3-Buten-2-yl Acetate at $80 \pm 0.1^\circ\text{C}$.^a

Time, hr.	P, m./kg.	M, m./kg.		% Polymer		Ratio T/E
		T	E	T	E	
2.12% Bz_2O_2						
0.0	0.0876	8.62	8.60	0.0	0.0	
2.5	0.0535	7.95	7.48	7.8	13.0	0.60
5.0	0.0327	7.54	6.73	12.5	21.7	0.58
24.0		6.87	5.90	20.3	31.4	0.65
5.09% Bz_2O_2						
0.0	0.2110	8.35	8.32	0.0	0.0	
2.5	0.1160	6.98	6.00	16.4	27.9	0.59
5.0	0.0596	6.23	4.56	25.4	45.2	0.56
24.0		5.04	3.93	39.6	52.8	0.75
9.86% Bz_2O_2						
0.0	0.4080	7.97	7.90	0.0	0.0	
2.5	0.1880	5.52	5.02	30.7	36.5	0.84
5.0	0.0885	4.38	3.71	45.0	53.1	0.84
24.0		3.26	2.40	59.1	69.6	0.85

^a Here T = data obtained by titrating residual unsaturation, and E = data obtained by evacuating reaction mixture to constant weight.

The polymer or nonmonomer content obtained by evacuation is higher than that obtained by titration. The unsaturation decreases as the reaction proceeds and the values obtained by titration correspond to those obtained by evacuation more closely as the initial catalyst concentration increases. At the lower initial catalyst concentration approximately one-

third of the nonmonomeric material is unsaturated, while at the higher initial catalyst concentration approximately one-fifth of the nonmonomeric material is unsaturated.

dM/dC and \overline{DP}

The constance of dM/dC , i.e., the disappearance of monomer as a linear function of the disappearance of peroxide, characteristic of allylic polymerization, is observed in the polymerization of 3-buten-2-yl acetate (Fig. 2). The data utilized in the plot of dM/dC are that obtained by evacuation and correspond to nonmonomeric material.

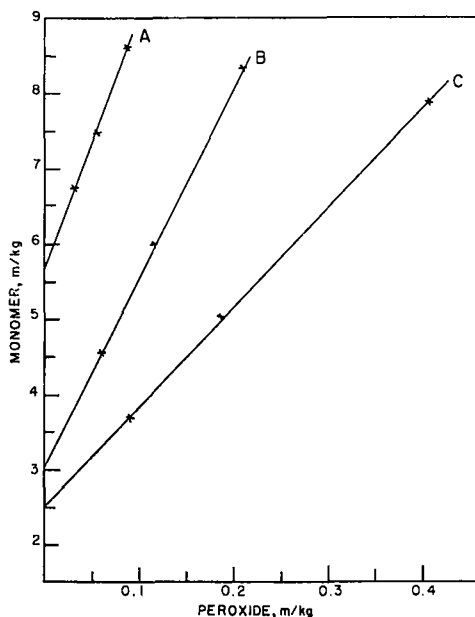


Fig. 2. Monomer concentration plotted against peroxide concentration in bulk polymerization of 3-buten-2-yl acetate with benzoyl peroxide at 80°C.: A, 2.12% Bz_2O_2 ; B, 5.09% Bz_2O_2 ; C, 9.86% Bz_2O_2 .

TABLE IV
Summary of Constants in the Polymerization of 3-Buten-2-yl
Acetate at $80 \pm 0.1^\circ C$.

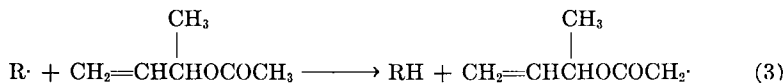
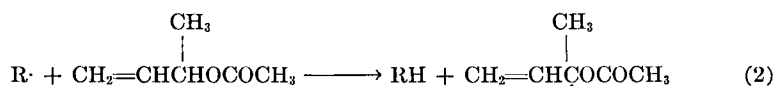
Initial wt. % Bz_2O_2	k_1 hr. ⁻¹ (decompd. Bz_2O_2)	dM/dC	\overline{DP}	% conversion, 48 hr.
2.12	0.197	32.7	2.84	32.3
5.09	0.252	24.8	2.81	54.3
9.86	0.305	13.1	2.81	71.1
2.82 ± 0.01				

The degree of polymerization is nearly constant and independent of the initial catalyst concentration. The average \overline{DP} is 2.8 as compared to a \overline{DP} of 12–13 in the polymerization of allyl acetate.

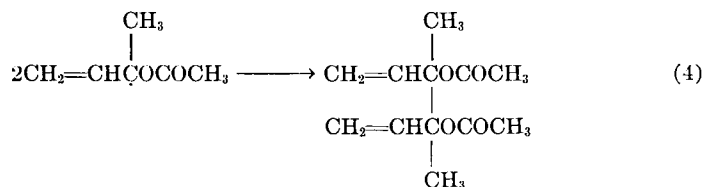
The values of dM/dC , \overline{DP} and other constants in the polymerization of 3-buten-2-yl acetate are summarized in Table IV.

DISCUSSION

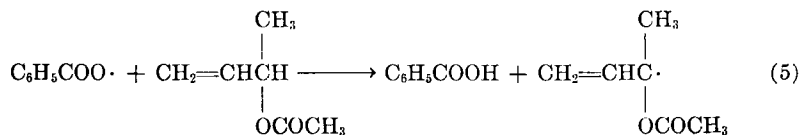
The variation in the rate of decomposition of benzoyl peroxide in polymerizing 3-buten-2-yl acetate, as a function of initial peroxide concentration, and the comparison of the values of k_1 in both allyl and α -methylallyl series (Table II) indicates considerable induced decomposition of peroxide. This implies the presence of relatively long-lived radicals such as those resulting from hydrogen abstraction.

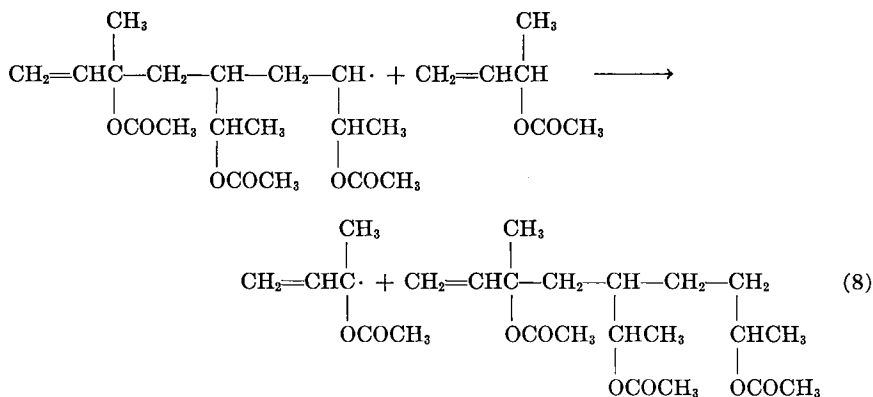
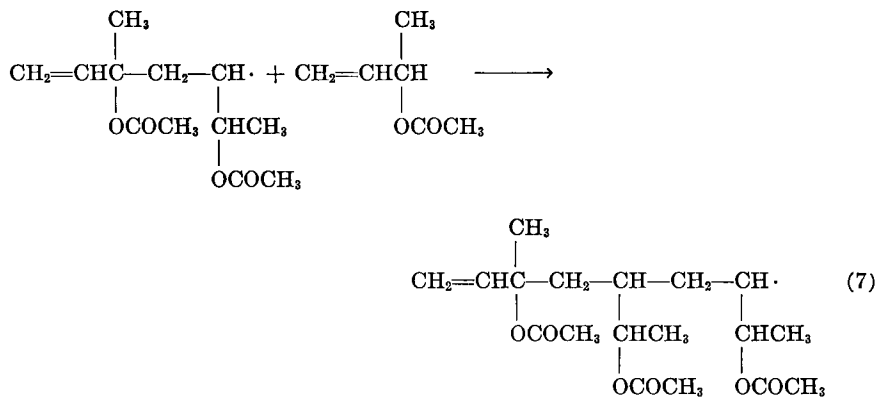
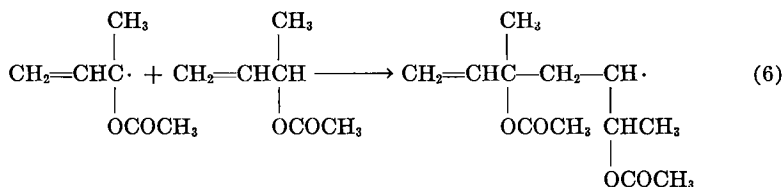


The attacking radical may be a benzoyloxy radical derived from the decomposition of peroxide or a growing chain radical. If the only reaction which these monomer-derived radicals could undergo was dimerization, e.g.



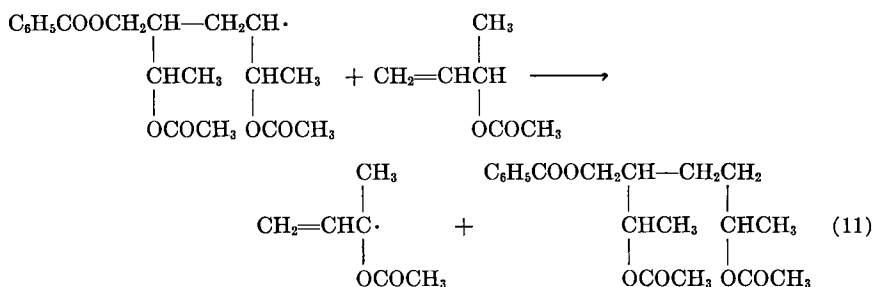
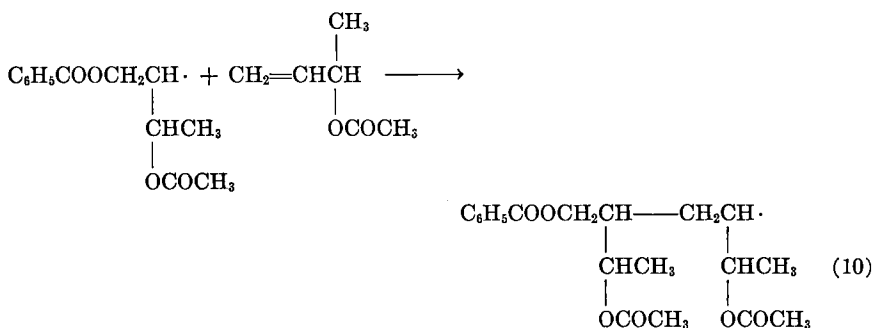
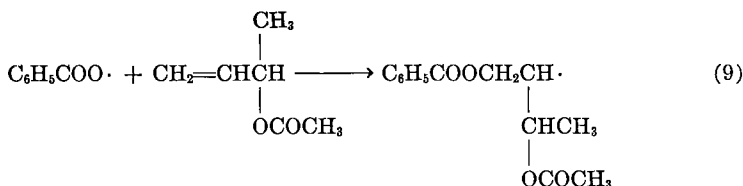
then the determination of unsaturation would indicate the retention of double bonds throughout the polymerization. Since unsaturation decreases as the polymerization proceeds, a further reaction of the radicals from reactions (2) and (3) must involve the consumption of double bonds. The value of 2.8 for the \overline{DP} indicates that a trimer may be formed to a considerable extent. In the case of 2% initial peroxide concentration the titration values are approximately two-thirds of the evacuation values. This corresponds to one double bond for every three monomer units consumed and may be explained by the following series of reactions:





By this sequence a trimer is formed which contains one double bond, corresponding to both the $\overline{\text{DP}}$ and the unsaturation data. Since one catalyst fragment yields a trimer as well as a radical arising by hydrogen abstraction from the monomer, the high consumption of monomer and the high dM/dC are explained. The radical formed in reaction (8) is the same as that formed in reaction (5) and can continue the sequence of reactions (6)–(8). Thus, a small number of catalyst fragments are responsible for the consumption of considerable amounts of monomer. The radicals formed in reactions (5) and (8) can induce the decomposition of peroxide to yield the high k_1 value obtained.

As the catalyst concentration increases the unsaturation decreases. This implies that with a greater number of catalyst fragments present, effective vinyl polymerization can accompany the previous sequence.



Here, two monomer units have been consumed with one peroxide fragment to yield a saturated molecule whose molecular weight corresponds to a trimer. Since the benzoyloxy fragment has a molecular weight of 121, and a monomer unit has a molecular weight of 114, the determination of molecular weight would indicate a catalyst fragment endgroup as a monomer unit. Since $\overline{\text{DP}}$ is a statistical value, chains containing three and even more monomer units would be balanced by chains containing one endgroup and one or more monomer units. The sequence of reactions (9)–(11) accompanied by the sequence (5)–(8) would result in the consumption of monomer to yield high conversions and high dM/dC with decreased residual unsaturation. Further, a high concentration of α -methylallyl radicals would result from an increase in reactions (8) and (11) and yield more induced decomposition of peroxide. The fact that tetramers and higher units are balanced by smaller chains in the determination of molecular weight holds in sequence (9)–(11) as well as (5)–(8). The allylic radical participating in these reactions may be that radical derived from the acid portion of the ester. Probably both radicals take part in these reactions.

The scheme postulated in reaction (6) and the proposed disposition of the radicals from reactions (8) and (11) implies the existence of considerable

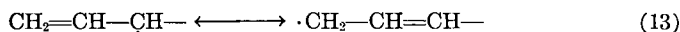
effective chain transfer rather than degradative chain transfer. As shown in the previous paper,³ Sakurada and Takahashi⁴ have postulated a kinetic scheme and arrived at the following equation for the determination of the fraction of degradative chain transfer in the total transfer reactions:

$$k_D/(k_D + k_T) = 2 \overline{DP}/([dM/dC]_0 + 2) \quad (12)$$

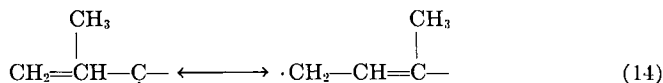
Extrapolating the straight line obtained by plotting the values of dM/dC versus the catalyst concentration⁴ yields a value of 38.1 for $[dM/dC]_0$ in 3-buten-2-yl acetate. Substituting this and the average \overline{DP} value of 2.82 in eq. (12) yields 0.138 for the value of $k_D/(k_D + k_T)$. This implies that 86% of the total transfer reaction in the polymerization of 3-butene-2-yl acetate is effective chain transfer and is in accordance with the polymerization schemes outlined previously. This amount of effective chain transfer compares with approximately 24% effective transfer in the polymerization of allyl acetate and is actually higher than that obtained with any allylic monomer.³

At this point it is of interest to compare the benzoyl peroxide catalyzed polymerization of 3-buten-2-yl acetate and allyl acetate. The former results in a higher $[dM/dC]_0$ (38.1 versus 32.3³) and a lower \overline{DP} (2.8 versus 12–14). The low \overline{DP} is related to the greater tendency for the substituted allylic monomer to permit hydrogen abstractions which result in chain termination. This may be due to the fact that the electron-donating tendency of the methyl group enhances the removal of hydrogen. However, after the abstraction of hydrogen the predominant form of the resultant resonance stabilized radical may be more reactive than the corresponding allyl radical so that effective chain transfer is involved and results in higher conversions and a higher $[dM/dC]_0$.

The structures of the two radicals involved provide a clue to the greater reactivity of the substituted form. In the allyl ester the following resonance stabilization exists



In the α -methylallyl ester we have



In eq. (13) the form on the left is the more stable secondary radical and therefore may be the predominant form. In eq. (14) the electron-donating methyl group would result in the predominant form being the form at the right, i.e., the primary radical. Since the primary radical would be more reactive than the secondary radical, the radical in the α -methylallyl ester would have a greater tendency to participate in addition to double bonds and is therefore a participant in effective chain transfer.

POLYMERIZATION OF 3-BUTEN-2-OL

The bulk polymerization of 3-buten-2-ol (methyl vinyl carbinol) was investigated using benzoyl peroxide as the catalyst at 80°C.

TABLE V
 Polymerization of 3-Buten-2-ol at $80 \pm 0.1^\circ\text{C}$.

Time, hr.	Peroxide m./kg.	Monomer m./kg.	% polymer
2.04% Bz_2O_2			
0.0	0.0816	9.86	0.0
0.5	0.0565	9.65	2.1
1.0	0.0378	0.59	2.7
2.5	—	9.43	4.4
5.0		9.41	4.6
24.0		9.39	4.7
4.18% Bz_2O_2			
0.0	0.1740	9.61	0.0
0.5	0.0855	9.41	2.1
1.0	0.0540	9.32	3.0
2.5	—	9.16	4.7
5.0		9.12	5.1
24.0		9.10	5.3
9.77% Bz_2O_2			
0.0	0.4980	9.04	0.0
0.5	0.2180	8.90	1.7
1.0	0.1480	8.81	2.0
2.5	—	8.44	6.7
5.0		8.44	6.7
24.0		8.44	6.7

As anticipated from the results with allyl alcohol,⁵ the rate of decomposition of benzoyl peroxide in 3-buten-2-ol is extremely rapid and the conversion of monomer to polymer is extremely low. These two effects,

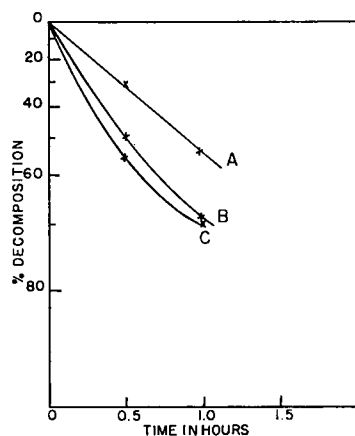


Fig. 3. Decomposition of benzoyl peroxide in polymerizing 3-buten-2-ol at 80°C .: A, 2.04% Bz_2O_2 ; B, 4.18% Bz_2O_2 ; C, 9.77% Bz_2O_2 .

however, are related in that the catalyst is so rapidly consumed that monomer consumption levels off in a very short time. Further, the chain transfer tendencies in the monomer, from the allylic position as well as the hydroxyl group, would terminate chain growth. The data in the attempted polymerization of methyl vinyl carbinol are summarized in Table V, and the decomposition of peroxide is plotted in Figure 3.

The various constants obtained in the polymerization are summarized in Table VI.

TABLE VI
Summary of Constants in Polymerization of 3-Buten-2-ol
at $80 \pm 0.1^\circ\text{C}$.

Initial wt. % Bz_2O_2	k_1 hr. ⁻¹ (decompd. Bz_2O_2)	$\overline{\text{DP}}$	dM/dC
2.04	0.772	2.20	4.58
4.18	1.17	2.19	2.74
9.77	1.21	2.16	2.50

The data summarized in Tables V and VI are based on titration values. However, in this case evacuation and titration data are in good agreement and if anything the former are a little lower.

Initial wt. % peroxide	% polymer, 24 hr.	
	evacuation	titration
2.04	4.72	4.75
4.18	5.24	5.30
9.77	6.70	6.75

This implies that the polymer is essentially saturated or that, since little polymerization occurs, the method is not accurate enough to detect differences.

The values for dM/dC have little significance as far as a calculation of effective chain transfer is concerned since the extremely rapid decomposition of peroxide makes the denominator very large.

EXPERIMENTAL

Method of polymerization. The polymerization procedure was the same as that previously used in the polymerization of allyl esters.¹

Determination of peroxide concentration. The concentration of benzoyl peroxide was determined by iodometric titration in glacial acetic acid after addition of potassium iodide.²

Determination of monomer concentration. The concentration of monomer was determined by addition of a bromate-bromide solution and back titration with sodium thiosulfate solution.²

The disappearance of monomer was further followed by stripping off all material volatile at 60–70°C. under 1 mm. pressure until constant weight was obtained. The residual weight was corrected for peroxide content.

Purification of polymer. The product from the exhaustive polymerization of the monomer was dissolved in benzene, extracted with aqueous potassium carbonate, dried with anhydrous potassium carbonate and concentrated and dried to constant weight at 100°C. at 1 mm. pressure, as previously described.¹

Determination of molecular weight. All molecular weights were determined cryoscopically in dioxane utilizing a Beckmann thermometer and mechanical stirring. The values of the freezing point depressions thus obtained were in each case the result of at least two checking determinations.

Preparation of monomers. 3-Buten-2-ol was prepared by the Grignard reaction between acrolein and methylmagnesium iodide at –10 to –20°C. The reaction mass was hydrolyzed with aqueous ammonium chloride solution, extracted with ether, dried over anhydrous potassium carbonate, and distilled twice through a packed column. The middle cuts were collected, b.p. 96–97°C., n_D^{25} 1.4137.

3-Buten-2-yl acetate was prepared by refluxing 72 g. (1 mole) of 3-buten-2-ol with 120 g. (2 moles) of acetic acid in the presence of 5 g. of *p*-toluenesulfonic acid for two hours. The reaction mixture was poured into water, the organic layer was separated, taken up in benzene, washed twice with a cold aqueous solution of potassium carbonate, and washed three times with cold water. The organic solution was dried over anhydrous potassium carbonate and sodium sulfate. The ester was distilled twice in the presence of nitrogen through a 4-foot column packed with Raschig rings and the middle fractions were collected, b.p. 110–110.7°C., n_D^{25} 1.4046 (reported⁶ b.p. 112°C., n_D^{20} 1.4048).

References

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Synopsis

The bulk polymerization of 3-buten-2-yl acetate with benzoyl peroxide as catalyst at 80°C. is characterized by degradative and effective chain transfer. Effective chain transfer constitutes 86% of the total transfer reactions. The polymerization results in a polymer with a DP of 2.8, independent of initial catalyst concentration, and in any given polymerization the disappearance of monomer is a linear function of the disappearance of peroxide, i.e., dM/dC is constant, and decreases linearly with increasing catalyst concentration, extrapolating to 38.1 at zero catalyst concentration. The values of dM/dC and conversion to polymer are higher with 3-buten-2-yl acetate than with allyl acetate. The polymer from the α -methylallyl ester contains approximately one double bond for every three monomer units at 2% peroxide concentration. The de-

composition of benzoyl peroxide in 3-buten-2-yl acetate is more rapid than in the allyl ester and is characterized by considerable induced decomposition. The decomposition of peroxide in methyl vinyl carbinol is extremely rapid and the conversion of monomer to polymer is very low.

Résumé

La polymérisation en bloc à 80°C de l'acétate de 3-butène-2-yl à l'aide de peroxyde de benzoyl comme initiateur est caractérisée par un transfert de chaîne dégradant et effectif. Le transfert de chaîne effectif constitue 86% du total des réactions de transfert. La polymérisation fournit un polymère de DP égal à 2,8, indépendamment de la concentration initiale en initiateur. Dans chaque polymérisation la vitesse de disparition du monomère est une fonction linéaire de la vitesse de disparition du peroxyde c.a.d. dM/dC est constant et décroît linéairement en fonction de l'augmentation de la concentration en initiateur. La valeur extrapolée à concentration nulle en initiateur d'élève à 38.1. Les valeurs de dM/dC et de la vitesse de conversion en polymère sont plus élevées pour l'acétate de 3 butène-2-yl que pour l'acétate d'allyle. Le polymère obtenu au départ de l'ester d' α -méthyl-allyle contient approximativement 1 double liaison pour trois unités monomériques à concentration en peroxyde de 2%. La décomposition du peroxyde de benzoyl dans l'acétate de 3-butène-2-yl est plus rapide que dans l'ester allylique et est caractérisée par une décomposition induite considérable. La décomposition du peroxyde dans le méthyl-vinyl carbinol est extrêmement rapide et le taux de conversion du monomère en polymère est très bas.

Zusammenfassung

Charakteristisch für die Polymerisation von 3-Buten-2-ylacetate in Substanz mit Benzoylperoxyd als Katalysator bei 80°C ist das Auftreten einer verzögernden und einer nicht verzögernden Kettenübertragung. Die nicht verzögernde Kettenübertragung erreicht 86% der gesamten Übertragungsreaktion. Die Polymerisation liefert, unabhängig von der Anfangskonzentration des Katalysators, ein Polymeres mit einem DP von 2,8 und bei jeder Polymerisation ist der Verbrauch des Monomeren eine lineare Funktion des Peroxydverbrauches, d.h. dM/dC ist konstant und nimmt mit steigender Katalysatorkonzentration linear ab, wobei eine Extrapolation auf die Katalysatorkonzentration Null den Wert 38,1 liefert. Die Werte von dM/dC und die Ausbeute an Polymerem sind bei 3-Buten-2-ylacetat höher als bei Allylacetate. Das Polymeres des α -Methylallylester enthält angenähert eine Doppelbindung auf drei Monomereinheiten bei einer Peroxydkonzentration von 2%. Die Zersetzung von Benzoylperoxyd verläuft in 3-Butenylacetat rascher als im Allylester und ist durch einen beträchtlichen Anteil an induzierter Zersetzung charakterisiert. Die Zersetzung des Peroxyds in Methylvinylcarbinol hat eine extrem grosse Geschwindigkeit und es findet nur eine sehr geringe Umwandlung des Monomeren ins Polymere statt.

Received June 12, 1959