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Divinylbutyral. I. Mechanism of Polymerization

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ABSTRACT

New results on the cyclic free radical polymerization of divinylbutyral (DVB) suggest that initiation occurs via hydrogen abstraction resulting in a multifunctional growth with up to 45% of abnormal reaction steps. While the rates of polymerization obeyed a square-root relationship to initiator concentration, the molecular weights were not found to be related to this quantity. Temperature-dependent isomerizations to ester and ketal and a cross-linking at earlier conversions at lower temperatures support a polyfunctional propagation terminated by recombination. Chain transfer constants to additives appeared to be among the highest reported for vinyl monomers. This characterizes DVB as a monomer of very high radical activity but possessing an unusually easily abstracted hydrogen atom.

INTRODUCTION

Divinyl acetals and their polymerizations were first reported in 1942 [1] in the patent literature. A cyclic inter-intra-molecular

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mechanism of propagation was clearly formulated there to explain the formation of soluble thermoplasts from nonconjugated dienes. Cyclic polymerization mechanisms were, however, recognized only in the mid-1950s, and divinyl acetals and their polymers were rediscovered in 1960 by Russian authors [2, 3].

The present paper covers an investigation of the polymerization variables of divinylbutyral (DVB) which was singled out because of the structural similarity of its polymer with polyvinylbutyral, the commercial safety glass interlayer. The application of monomer of ultrahigh purity in this work resulted in revisions of previously reported data on the polymerization of DVB.

The results of the study of the unusual structure of the polymer form the second part of this paper.

RESULTS AND DISCUSSION

Monomer Synthesis and Purification

The synthesis of DVB by dehydrochlorination of di(2-chloroethyl) butyral was carried out similarly as in Refs. 1 and 2. Multiple fractionations on a spinning band column from sodium benzophenone ketyl resulted in monomer of less than 20 to 30 ppm combined impurities; in one case of less than 5 ppm impurities (based on benzene as a reference). The boiling point of this grade of monomer at atmospheric pressure was found higher by 3° than that reported in the literature, but decreasing with time of reflux, indicating thermal decomposition. This thermal instability was confirmed by a series of vapor pressure chromatography (VPC) analyses at varying column temperatures where a safe working temperature of 70 to 80°C was established. The temperatures of distillation, polymerization, and of DVB analysis were adjusted correspondingly. Only after these parameters had been established was it possible to arrive at reproducible kinetic data.

Polymerization

The rate of polymerization in bulk was found to follow the normal proportionality to the square root of initiator concentration (Fig. 1), contrary to earlier data on the analogous polymerization of

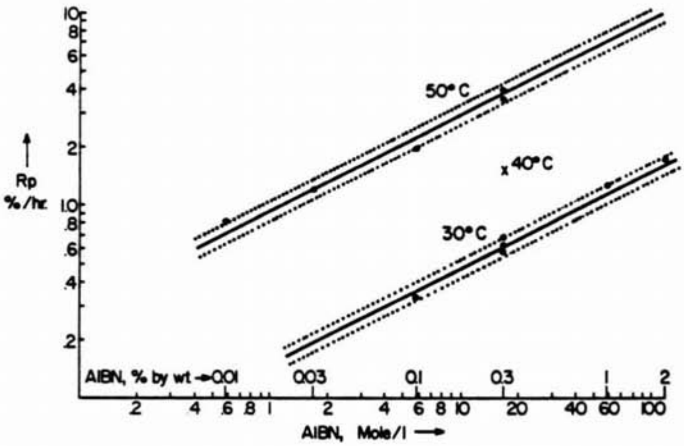


FIG. 1. Rate of polymerization of DVB in bulk. Catalyst: Azobisisobutyronitrile.

divinylformal where a relationship to the 3/4 power in initiator concentration has been reported [4]. The rate constants with azobisisobutyronitrile as initiator were 0.285 ± 10% at 30°C and 1.85 ± 10% at 50°C ($\text{mole}^{1/2}\text{liter}^{-1/2}\text{hr}^{-1}$ (Table 1). The data were obtained by varying the initiator concentration over a twentyfold range and using monomer from different batches purified to less than 30 ppm combined impurities.

Contrary to earlier reports on divinyl acetals (e.g., Ref. 4), the molecular weights were found to be independent of the concentration of the initiator over this same range, expressed as intrinsic viscosities (Table 1). Moreover, they probably exceeded values of 200,000 compared to reported data which seemed to range from 5,000 to 20,000. However, the molecular weights were dependent on the temperature of polymerization but independent of conversion. It was also noticed that at higher conversions gel formation took place, attributed to cross-linking. It was unexpected that cross-linking occurred at an earlier degree of conversion the lower the temperature of polymerization was (Table 2).

This is contrary to the expected trend in cyclic polymerizations where it is established that the noncyclic propagation requires a higher activation energy and thus should result in earlier

TABLE 1. Bulk Polymerizations of DVB[a]

Temp (°C)	[AIBN] × 10^{-3} (mole × liter^{-1})	k ($\text{mole}^{1/2}\text{liter}^{-1/2}\text{hr}^{-1}$)	Yield (% after hours)		η (benzene)
32	117.6	0.303	10.35	6.0	1.0
			17.06	10.55	0.95
			40.4	26.0	1.05
32	58.8	0.312	9.85	8.0	0.90
			21.9	18.3	1.30
			35.9	32.6	1.10
32	16.8	0.310	41.6	66	Gel point
32	16.8	0.280	12.25	18.9	0.98
			20.5	32.0	1.20
			37.5	68.0	1.15
32	16.8	0.285	11.7	20.0	0.93
32	5.88	0.255	10.7	32.0	1.25
			19.0	68.0	1.10
40	16.8	0.693	10.5	7	0.54
			28.3	19	0.65
50	19.6	2.04	15.3	3.2	0.48
50	16.8	1.780	28.2	8	0.56
50	16.8	1.67	60	18	Gel point
50	1.68	1.77	29	27	0.62
50	0.588	2.06	20.7	27	0.44

[a] Rate during first 5-10% conversion, excluding induction periods. DVB from five different batches was used. Bulk = 5.88 moles/liter.

TABLE 2

Temp (°C)	Initiator	Approx gel point (%)
-50	$B(n\text{-}Bu)_3/O_2$	17
0	$B(n\text{-}Bu)_3/O_2$	25
32	AIBN	41
50	AIBN	60
140	tert-Bu-peroxide	100

cross-linking at a higher temperature [5]. This was taken as an indication for a mode of cross-linking different from that reported for other dienes. It was then found that the polydivinylbutyral (PDVB) obtained in this study did not contain carbon double bonds according to its IR spectrum (which, however, showed two carbonyl absorptions). If cross-linking had occurred via a typical noncyclic mechanism, then some of the nonparticipating double bonds would have remained unreacted and identifiable.

Monomers of lesser purities yielded polymers of much lower molecular weights. Their degrees of polymerization were often found to increase with conversion. This suggested a slow consumption of terminating or chain-transferring impurities, and has been reported for the polymerization of divinylformal [4] but without giving credit to the effect of impurities in the monomer.

Effect of Additives and of Solvents

An attempted copolymerization with styrene (purified from sodium benzophenone ketyl) at 50°C using azobisisobutyronitrile as an initiator and employing four different ratios of the comonomers showed that DVB did not copolymerize, contrary to S. G. Matsoyan's reports [6]. The homopolymerization of styrene was slowed down by increasing amounts of DVB (Table 3).

Infrared spectra of the polymers were identical to polystyrene in all respects.

TABLE 3. Attempted Copolymerization with Styrene
(Temp: 50°C; [AIBN]: 8.4×10^{-3} mole/liter; time: 51 hr)

Mole ratio, DVB/styrene	Yield (% of styrene)
3/1	24
1/1	10.3
1/3	41.8
1/9	39.1

Screening of several additives and solvents showed that all depressed the molecular weights, apparently due to chain transfer reactions. Several were selected for further study to see whether polymerizations in solvents would be feasible and benefit the physical properties of the polymer. The effect of benzene and of tert-butanol on the degree of conversion and on molecular weights is plotted in Fig. 2. It is apparent that up to 3.5 or 4 mole/liter of DVB, the

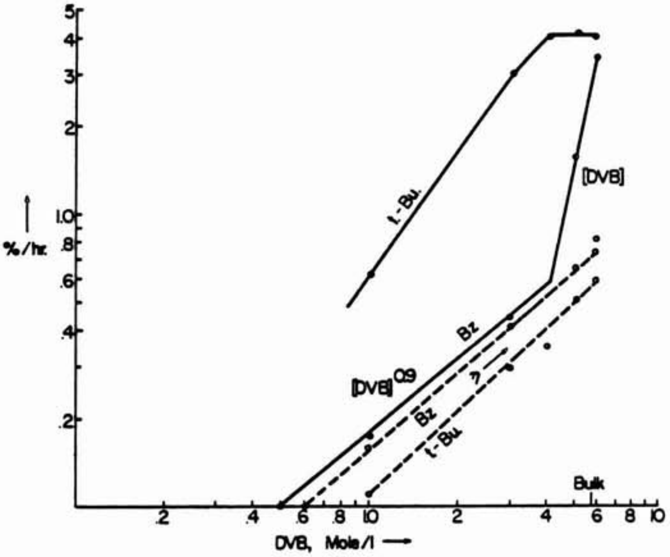


FIG. 2. Rate of conversion of DVB in benzene and in tert-butanol. AIBN: 1.68×10^{-2} mole/liter. Temperature: 52°C.

rates of polymerization followed the usual approximate first power relationship in monomer concentration. In the case of benzene, the rate increased with the fifth power of monomer concentration above 4 moles/liter of DVB, while with tert-butanol the rate appeared independent of solvent above 3.5 moles/liter of DVB. The abnormal slowdown in rates at a lesser monomer concentration may indicate that the radicals formed in transfer to benzene were less reactive than monomer radicals. The changes in the order of the reaction lack explanation, but similar phenomena have been observed with other monomers such as acrylic anhydride [7] or trans-cinnamate [8].

The chain transfer constants, C_s, were obtained graphically from the data in Table 4.

TABLE 4. Chain Transfer of DVB at 50°C
(Catalyst: 16.8×10^{-3} mole/liter AIBN

Additive (A)	Ratio, A/DVB	Conversion (%/hr)	$[\eta]$	$10^3\overline{P}_n^{-1}$
Blank	0	4.1	0.76	2.1
Benzene	0.33	1.5	0.66	2.65
Benzene	1.82	0.5	0.43	5.35
Benzene	9.25	0.2	0.16	27.17
tert-Butanol	0.32	4.3	0.51	4.05
tert-Butanol	0.85	4.1	0.44	5.13
tert-Butanol	1.73	3.1	0.36	7.0
tert-Butanol	8.86	0.6	0.14	34.7
2-Propyl-1,3-dioxolane	0.01	4.35	0.52	3.92
	0.05	3.75	0.47	4.63
	0.1	3.75	0.27	11.49
n-Butanal	0.01	3.48	0.36	7.14
	0.05	2.58	0.18	22.61
	0.1	2.37	0.14	33.90
N,N-Dimethylaniline	0.001	4.00	0.56	3.47
	0.01	2.87	0.46	4.81
	0.05	<1	0.43	5.47

They are approximate because the degrees of polymerization were calculated from intrinsic viscosities which were related experimentally to $\overline{M}_n$ values only up to 30,000 (using a Fisher osmometer).

Furthermore, with most additives a depression of the rate of polymerization was observed (Table 4) which is known to distort the measured chain transfer constants. Nevertheless, these constants are high compared with those for styrene and vinyl acetate [9] (Table 5).

TABLE 5

$C_s \times 10^3$	DVB	Styrene	Vinyl acetate
Benzene	2.77	0.001	0.1-0.3
tert-Butanol	3.72	0.66	0.05-0.1
n-Butanol	350	0.65	65-100
2-Propyl-1,3-dioxolane	70.8	-	-
N,N-Dimethylaniline	106	1.2-5.3	26

The data show that the radical formed from DVB is ten to twenty times more reactive than that formed from vinyl acetate and comparable to the ethylene radical in its reactivity towards benzene ($C_s = 1.8 \times 10^{-3}$).

It was also found that a polymerization of DVB in carbon tetrachloride as a solvent resulted in the formation of hydrogen chloride and subsequent destruction of the monomer due to ionic attack on the acetal linkage. The evolution of hydrogen chloride showed that hydrogen was abstracted from DVB or PDVB by chlorine radicals. The normal attack of free radicals on carbon tetrachloride results in a chlorine-terminated telomer and in trichloromethyl radicals, but not in chlorine radicals except in systems containing allylic hydrogen [10]. The formation of chlorine-free radicals shows that the DVB radical is capable of an indiscriminate attack on a carbon-chlorine bond. It also shows that DVB or its polymer contains hydrogen atoms which can be easily abstracted, comparable to allylic hydrogen atoms.

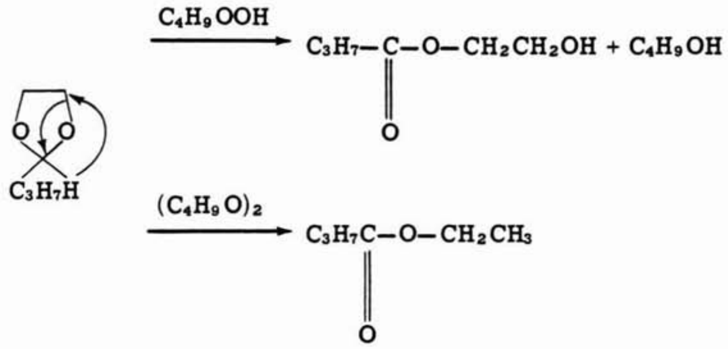
Mechanism

The above results suggest a reaction mechanism which differs considerably from that of other cyclic polymerizations. For example, the observed independence of the degree of polymerization ($\overline{DP}$) from the concentration of initiator could be explained by a polyfunctional growth reaction, provided termination occurs by recombination as indicated by the absence of unsaturation in PDVB. In such a system, the $\overline{DP}$ is then proportional to the ratio of rates of propagation to transfer [11]. Since transfer reactions require higher activation energies, this value decreases at higher temperatures.

The possibility of a polyfunctional growth is dependent on initiation and transfer steps which, therefore, were studied next. In order to determine the mode of free radical attack on DVB and on PDVB, the reaction of the model compound 2-propyl-1,3-dioxolane (distilled from Na-benzophenone) with large amounts of initiators was studied.

In the case of azobisisobutyronitrile (molar ratio dioxolane/AIBN = 8/1, 72 hr, 70°C, in Ar atmosphere), the main products were unchanged dioxolane and tetramethylsuccinonitrile from recombination. Approximately 12% of the lower boiling material was a mixture of a carbonyl containing product and isobutyronitrile, indicating that some hydrogen abstraction had taken place. A further separation of products was not attempted due to complication by the easily sublimable succinonitrile.

When the reaction was repeated with technical grade di-tert-butyl peroxide, containing some tert-butylhydroperoxide (molar ratio dioxolane/peroxide = 5/1, 72 hr, 110°C, Ar atmosphere), the main products were tert-butanol, ethylbutyrate, and hydroxyethylbutyrate, proving free radical attack on the 2-hydrogen exclusively. Several similar isomerizations have been reported in the literature [12].



After spinning band fractionation, a material balance was established with the aid of VPC techniques, comparing IR and mass spectra to those of authentic samples (Table 6).

TABLE 6

	Mole-% recovered
Ethylbutyrate	39.8
Hydroxyethylbutyrate	22.2
Propyldioxolane	15.6
Total recovered dioxolane derivatives	77.6
tert-Butanol (based on di-tert-Bu-peroxide)	68
tert-Butanol (based on tert-Bu-hydroperoxide)	84.3
Unidentified (5 compounds by VPC)	7.5% by weight
Unaccounted	15.5% by weight

Part of the unaccounted material escaped as a gas during the reaction, indicating destruction of some molecules.

The isomerization could also be produced in the polymer. A sample of PDVB was refluxed in tert-butanol with di-tert-butylperoxide for 3 days. Over one-third of the acetal units had isomerized to ester (saponification number 145.0), and the polymer had turned brittle and higher melting (~150°C). The IR spectrum was in agreement with an ester structure. It was then established that the same isomerization occurred during normal polymerizations at different temperatures to varying degrees. This showed that isomerization to the ester is favored at higher temperatures:

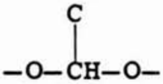
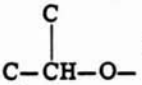
Polymerization temp (°C):	115	50	0	-50
Ester/monomer:	1/5	1/23-32	1/36	1/59

The data were calculated from saponification numbers.

The monomer was subsequently subjected to a similar reaction, as with the model compound dioxolane and PDVB above.

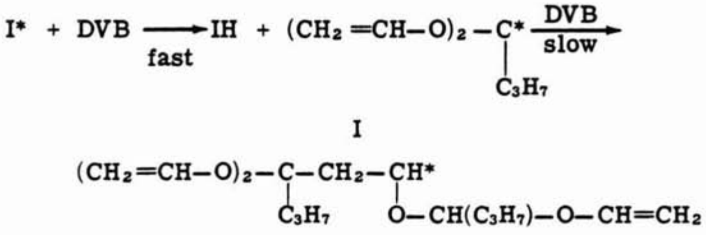
Slow addition of DVB (0.33 mole) to di-tert-butylperoxide (0.13 mole) at 110°C, during 25 hr in Ar atmosphere, has yielded:

tert-Butanol	9% of peroxide
Nonreacted peroxide	75% of peroxide
Nonreacted DVB	10.7% of DVB
Polymer	84.4% of DVB
Total losses	6.7% by weight
Non-identified volatiles	<1%

The polymer was subdivided by fractional precipitation into methanol. The IR spectra of all fractions showed pronounced carbonyl absorptions and other minor differences compared with ordinary PDVB. Notably, even the most soluble portion (19.7% solution in cold methanol) did not contain tert-butoxy groups according to its NMR and IR spectra and elemental analysis (theory for PDVB: C, 67.55; H, 9.93. Found: C, 67.30; H, 9.68%). The NMR spectrum indicated a decrease by 25% in acetal protons  $-O-\overset{\displaystyle C}{\overset{|}{C}}H-O-$ and by 37.5% in ether protons  $C-\overset{\displaystyle C}{\overset{|}{C}}H-O-$ most of which were shifted to $-CH_2-$ (or $-CH_2-O-$) positions, based on the methyl group as a standard. Base saponification of this oligomer required 101.4 mg KOH/g, indicating that every fourth DVB had been converted into an ester.

The total oligomers had a molecular weight (Fisher osmometer) of 3416 and the cold methanol soluble portion of 1026, corresponding to a heptamer. If the latter had contained one tert-butoxy group, the methyl protons would have comprised about 10% of all protons which is well detectable by spectral analyses. Thus it is considered established that the initiation occurred via hydrogen abstraction and not by addition of an initiator radical to the monomer, at least at these higher temperatures.

The actual formulation of the initiation mechanism is speculative and based on the assumption that the most reactive hydrogen is abstracted.



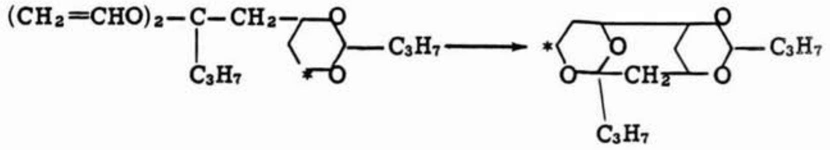
$$I^* + DVB \xrightarrow[\text{fast}]{} IH + (CH_2{=}CH{-}O)_2{-}\underset{\displaystyle C_3H_7}{\underset{|}{C^*}} \xrightarrow[\text{slow}]{DVB}$$

I

$$(CH_2{=}CH{-}O)_2{-}\underset{\displaystyle C_3H_7}{\underset{|}{C}}{-}CH_2{-}\underset{\displaystyle O{-}CH(C_3H_7){-}O{-}CH{=}CH_2}{\underset{|}{CH^*}}$$

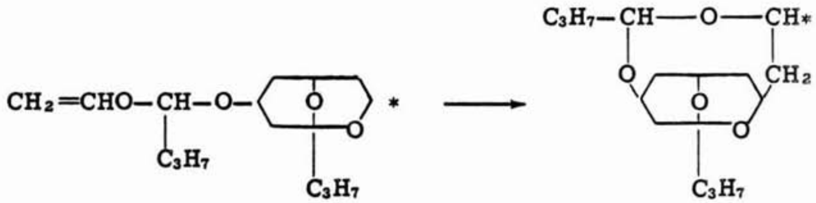
II

If intermediate II activates all of its three double bonds, a normal, monofunctional propagation would result (IIIa). However, after addition of one or two of its double bonds (IIIb and IIIc have equal probability), it has to acquire a seven (IIIa$_1$, derived from head to head addition) to ten (IIIa$_2$) ring conformation to add the third one, which is less favored.



IIIb

IIIa$_1$



IIIc

IIIa$_2$

Therefore, at least some additional monomer will add to IIIb or IIIc before its double bonds react, thus making them available for participation in other chain growth.

Similar anomalies as in the initiation are thought to exist in the propagation steps. It is estimated that at least 5%, and at higher temperatures up to 40%, of reaction steps are not a normal, cyclic propagation, nor a linear polymerization. This is supported by a number of facts.

First, the isomerization demonstrated above results in 2 to 20% of measured ester structures, depending on temperature.

Second, PDVB contains an estimated 5-20 mole-% of ketals, as indicated by Structures IIIa$_2$ and IIIc, for which evidence is presented in Part II of this paper. It is also shown there that the hydrolysis products are not pure polyvinyl alcohols.

The causes for abnormal propagation steps are thought to be related to the high reactivity of the DVB free radical, evidenced by the formation of hydrogen chloride from carbon tetrachloride and by the chain transfer constants, which are ten to twenty times higher than those of vinyl acetate. The transfer constants thus appear to be among the highest recorded for vinyl monomers.

As a consequence of high radical activity and the presence of allylic-type hydrogen in DVB, chain transfer is very frequent in bulk polymerizations and predominantly to the acetal hydrogen of the monomer rather than to polymer. This is probably because of the higher acidity of this hydrogen atom in DVB as evidenced by a down-field shift of its NMR when compared to PDVB or saturated analogs of comparable magnetic environment. A transfer to polymer is thought to also involve the acetal hydrogen atoms since it was found that a PDVB gel, swollen in tetrahydrofuran, can be instantaneously solubilized by addition of a few drops of concentrated hydrochloric acid. This shows that the transfer, with subsequent branching and cross-linking via recombination, could not have taken place at the carbon backbone of PDVB. It is suggested that hydrogen abstraction from the polymer at lower temperatures causes branching, and eventually, cross-linking, while at higher temperatures isomerization to the ester occurs. This is probable because of the relationship of the temperature of polymerization to the gel point (Table 2) and to the ester content as measured by the saponification number.

Terminations of kinetic chains are believed to occur via recombination, which in the case of normal, cyclic propagation steps, results in head-to-head structures. This is supported by the absence of unsaturation in PDVB and by the occurrence of cross-linking.

A termination of a polyfunctional growth reaction prior to cross-linking can be visualized only via a cyclic mechanism, or by combination with catalyst, solvent, or impurity fragments. Considering the high chain transfer constants, it is probable that the latter type is dominant, especially with impure DVB. Evidence for the formation of large cyclic structures during the polymerization of DVB is given in Part II.

EXPERIMENTAL

The following instruments were used in spectral analyses: a grating IR spectrometer from Perkin-Elmer, Model 521; a single-focusing mass spectrometer from Consolidated Electrodynamic Corp., Model 21-103-C; and an NMR spectrometer from Varian, Model A-60. The molecular weights were determined in a vapor pressure osmometer from Mechrolab, Inc., Model 302.

Purification of DVB

To obtain highest purity for kinetic studies, DVB was fractionated at 65°C at 28 torrs through a 4' spinning band column from sodium benzophenone ketyl until the combined impurities were below 10-20 ppm. Depending on starting purity, this required two to four distillations with a boil-up of 50-100 ml/hr and take-off ratios of 21/1 to 40/1 during removal of low boilers. The main cut was received at faster rates, leaving 5-10% of the total as a pot residue. It was found necessary to measure the purity with vapor phase chromatographs using a flame ionization detector, calibrated with benzene. Less sensitive chromatographs registered 0% impurities at the 50-100 ppm levels.

Polymerization of DVB at 32 and 50°

The appropriate amounts of AIBN were placed in two-neck flasks provided with a stopper and a three-way inlet stopcock. The air was replaced by argon by several evacuations. Highly purified DVB was added from a syringe through the stopcock against a flow of argon. The flask was immersed in a thermostated (±0.1°) bath. An argon flow through the stopcock was maintained throughout the polymerization. Samples were withdrawn periodically via syringes through the stopcock. Their refractive index n_D^{25} was measured to determine the rates of polymerization. Gravimetrically established conversions (%) were found related to n according to: $\% = 100(n - 1.4220)/0.0615$ within ±2% accuracy. After the desired degree of conversion was achieved, the mixture (after dilution with benzene in cases of high viscosities) was poured into a tenfold volume of methanol with fast agitation. It was subsequently reprecipitated three times from benzene into methanol and dried at 20 torrs/50° for 2 days and 16 hr at 0.5 torr/50°.

Reflux Temperature (145°)

Freshly purified DVB (882 g) and 9 g of di-tert-butylperoxide were heated under argon to 145° in a 2-liter flask equipped with a reflux condenser, stirrer, and argon inlet and outlet. The monomer must be heated slowly to reflux to prevent loss of material. The reaction was terminated after refluxing 1.5 hr by addition of 6 g of hydroquinone dispersed in 750 cc benzene. After cooling to room temperature, the solution was poured into 4 liters of methanol containing enough potassium hydroxide to raise the pH to 11. The solution became dark brown because of the formation of the potassium hydroquinone salt. The polymer precipitated as a viscous oil. This was washed twice with methanol and then placed in a Teflon-coated pan and dried as above. Yield 348 g (40%), intrinsic viscosity in benzene at 25°C was 0.21.

Polymerization of DVB at Room Temperature with the Monoperoxy Ester of Tri-n-butyl Boron as Initiator

Freshly purified DVB (2875 g) was cooled to 0° in a 5-liter flask using an ice bath. The flask was equipped with stirrer, argon inlet below the surface, argon outlet, thermometer, and rubber septum. The tri-n-butyl boron (5 g) was added slowly with a syringe through the septum. This was stirred 20 min. Then the oxygen was added 100 cc at a time from a syringe. The stoichiometric amount is 638 cc, but the reaction became so exothermic that only 300 cc could be added. With ice bath cooling, the temperature went to 35° in 25 min. The conversion at 45 min was 16.7%. The temperature gradually lowered to 3° after 2.5 hr when the conversion reached its maximum of 22%. The reaction was terminated when 4 g of hydroquinone and 2 liters of benzene were added. The solution was poured into 5 liters of methanol containing 10 g potassium hydroxide. The dark brown potassium hydroquinone salt formed. The polymer was filtered off and treated as above.

Yield 528 g (22%), intrinsic viscosity was 0.62 in benzene at 25°.

Polymerization of DVB at -50° with the Monoperoxy Ester of Tri-n-butyl Boron as Initiator

This polymerization was similar to number 3 above except that cooling was with Dry Ice-acetone. There was no noticeable exotherm and the stoichiometric amount of oxygen was added.

Yield after 2 days, 16%. Intrinsic viscosity in benzene at 25° was 0.32.

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