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Thermal degradation of vinylidene chloride/butyl acrylate copolymers

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Abstract

Vinylidene chloride/acrylate copolymers display a good barrier to the transport of small molecules (oxygen, carbon dioxide, water, etc.) as well as to flavor and aroma constituents of food items. For this reason, they occupy a place of prominence in the barrier plastic packaging industry. However, at process temperatures, these materials tend to undergo degradative dehydrochlorination. This is a typical radical chain process with distinct initiation, propagation, and termination phases and if unchecked can lead to the development of coloration which may be objectionable in some applications. To examine the influence of an aliphatic side chain on this process, a series of vinylidene chloride/butyl acrylate (4, 8, 12, 18, 20 wt.%) copolymers have been sythesized and fully characterized by chromatographic, thermal, and spectroscopic methods and by thermogravimetry. Increasing levels of butyl acrylate in the copolymer have little impact on the rate of initiation of degradation but do modestly decrease the propagation rate for the degradation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetry; Vinylidene chloride/butyl acrylate copolymers; Dehydrochlorination; Dichloromethylene reactivity

1. Introduction

Vinylidene chloride (VDC) copolymers have several outstanding properties, such as high crystallinity, resistance to non-basic solvents and most importantly extremely low permeability to a wide variety of gases [1,2]. However, a serious deficiency of these materials is thermal instability at melt-processing temperatures which leads to the formation of poly(chloroacetylene) sequences and gives rise to objectionable color. For many applications of VDC-containing polymers, such color development is undesirable and considerable effort has been made in an attempt to gain an understanding of the dehydrochlorination reaction and to devise methods by which it might be controlled or mitigated [3]. The dehydrochlorination is a typical radical chain process. Thermally-induced carbon–chlorine bond homolysis gives rise to a carbon–chlorine radical pair [4,5]. The chlorine atom so produced most typically abstracts an adjacent hydrogen atom to form hydrogen chloride and generate an allylic dichloromethylene unit in the polymer main chain, which may act as an initiation site for rapid sequential further dehydrochlorination (Scheme 1). Efficient trapping of chlorine atoms would interrupt propagation of the dehydrochlorination and lend stability to the polymer. Unfortunately, most radical stabilizers are inadequate for this purpose [3,4]. Any such hydrogen donating system must be more intimately associated with the polymer to be effective. It has been noted, for example, that polyethylene or polypropylene grafted to the polymer main chain may act as

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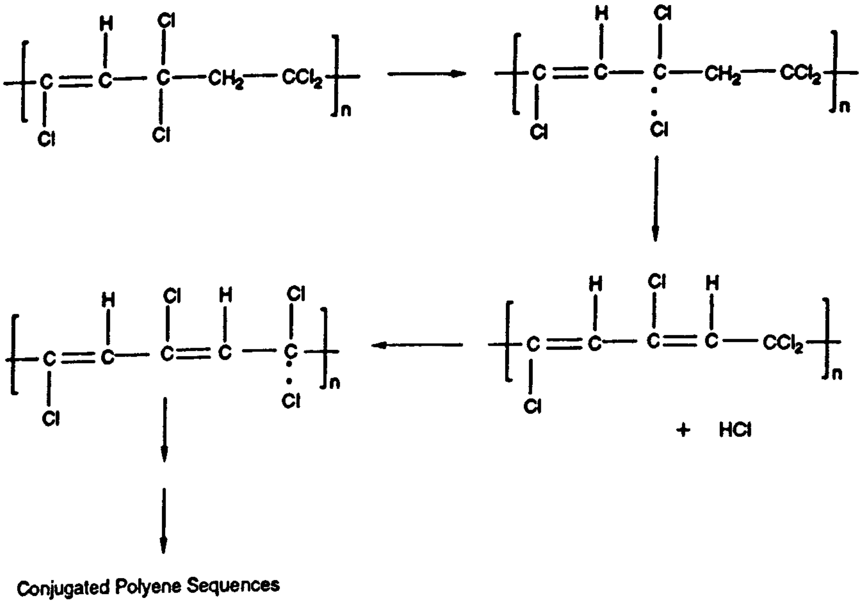


Scheme 1. Mode of degradation of vinylidene chloride polymers.

efficient hydrogen atom donors [6]. Based on this observation, it might be expected that incorporation into the polymer of acrylate derived from normal alcohols of several carbon atoms would have a stabilizing influence. In this instance, the thermal stability of copolymers of vinylidene chloride and butyl acrylate (four hydrogen-bearing carbon atoms in the side chain) has been examined by thermogravimetry.

2. Experimental

2.1. Materials

Vinylidene chloride/butyl acrylate (4, 8, 12, 18, and 20 wt.%) copolymers were prepared by suspension polymerization using methods previously described [7]. The copolymers were characterized by thermal (DSC, TGA), chromatographic (SEC), and spectroscopic (^1H and ^{13}C NMR) methods. They were random copolymers displaying a glass transition (T_g) between 0.99 (4% BA) and 8.4°C (20% BA). The two polymers of lowest butyl acrylate content, 4 and 8%, were semicrystalline with melt temperatures (T_m) of 183 and 159°C, respectively. To observe a sharp glass transition temperature, samples were held at 185°C for 75 s and quench cooled in liquid nitrogen prior to analysis. The unannealed polymer displayed melting behavior characteristic of vinylidene chloride copolymers. The glass transition temperatures reported are the averages of several determinations and are included in Table 1. Molecular weights were determined by size-exclusion chromatography. They were relative to narrow molecular weight polystyrene standards (Polymer Laboratories) using 0.25% weight/volume solutions in tetrahydrofuran (THF). Waters Associates modular chromatographic system which included model M-6000 pump and a model 410

Table 1
Thermal transitions for vinylidene chloride/butyl acrylate copolymers[a]

Butyl acrylate (wt.%)[b]	T_g (°C)	T_m (°C)
4	0.99	182.9
8	2.61	159.2
12	4.38	
18	7.84	
20	8.41	

[a] Determined by DSC.

[b] Weight percent monomer loaded.

Table 2
Molecular weight data for a series of vinylidene chloride/butyl acrylate copolymers[a,b]

Butyl acrylate (wt.%)[c]	M_n	M_w	M_z	M_w/M_n
4	42 567	85 927	144 970	2.02
8	44 699	89 869	150 760	2.01
12	44 304	89 676	150 675	2.02
18	54 835	131 791	242 686	2.40
20	56 896	139 926	259 862	2.46

[a] M_n: number average; M_w: weight average; M_z: z-average; M_w/M_n: molecular weight distribution.

[b] Determined by size exclusion chromatography.

[c] Weight percent of monomer loaded.

differential refractive index detector was used for this study. Two 5-micron mixed bed columns from Polymer Laboratories (No. 5M-M-35-59, 60) were used in series. Molecular weights for this set of polymers are presented in Table 2.

2.2. Degradation procedure

The thermal degradation of various vinylidene chloride copolymers was followed using a TA Instruments model 2950 TGA unit interfaced with a TA Instruments Thermal Analyst 2100 control unit. Polymer samples (15–20 mg) were loaded into a platinum sample pan. In a typical run, the TGA cell was swept with nitrogen at 50 ml/min for 30 min prior to the beginning of and during data collection. Weight loss was followed either as a function of temperature or time. A 5°C/min ramp was used; isothermal decomposition was followed at 180°C using the isotherm feature (temperature controlled on oven thermocouple) of the Thermal Analyst 2100 software. Temperature control for isothermal runs was ±0.02°C.

Dynamic experiments were used to follow qualitative differences in initiation and propagation as a function of comonomer loading, whereas isothermal runs were used to obtain first-order rate constants for initiation and propagation of dehydrohalogenation. Rate constants were taken as the slopes of the appropriate linear portions of the plot of $\ln[(w_\infty - w_0)/(w_\infty - w_t)]$ versus time; where w_∞, is the weight of the sample at infinite time (t_∞) taken as that weight which would remain after 37.62% of the initial vinylidene chloride component weight (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the copolymer had been lost); w_0 is the weight at time zero (t_0), that is, the time at which the first point was recorded and w_t is the weight at any time (t), during the run. This is illustrated for the degradation of 20% butyl acrylate copolymer Fig. 1. Data for decomposition in the early part of the run corresponding to initiation of degradation is replotted in Fig. 2, while similar data from late in the run where propagation of degradation is prominent, is displayed in Fig. 3. As can be seen, the fit in both cases is excellent.

3. Results and discussion

Alkyl pendant groups have been thought to add stability to vinylidene chloride copolymers [6]. These hydrogen-rich side chains were thought to serve as hydrogen atom donors for the scavenging of chlorine atoms produced during the thermal dehydrohalogenation in vinylidene chloride segments within the polymer. To test this suggestion, using an alkyl group of modest size, a series of vinylidene chloride/butyl acrylate (VDB/BA) copolymers of varying acrylate content (4–20 wt.%) has been prepared and examined by thermogravimetry. The potentially stabilizing influence of the alkyl group is depicted in Scheme 2.

The initial thermal event produces a carbon radical–chlorine atom pair. Intervention of the side chain to deliver a hydrogen atom to trap the chlorine atom before it is able to abstract an adjacent hydrogen atom from the main chain would effectively interrupt propagation of the degradative dehydrochlorination reaction and lend stability to the polymer (Scheme 3).

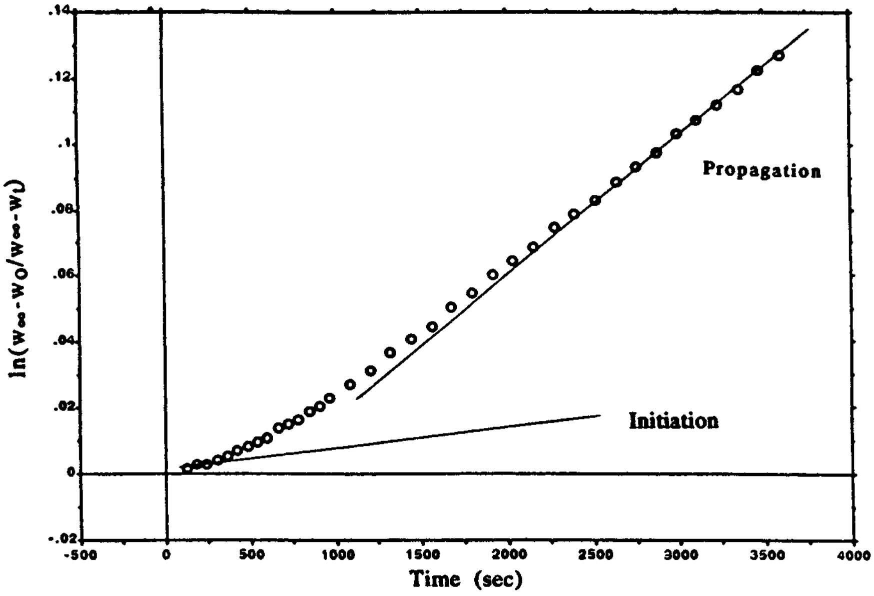


Fig. 1. Thermal degradation of a vinylidene chloride/butyl acrylate (20 wt.%) copolymer at 180°C.

Temperatures for the onset and maximum rate of degradation for the series of VDC/BA copolymers are collected in Table 3. As may be noted, there is no noticeable change in degradation onset temperature but the temperature of maximum degradation rate increases with increasing butyl acrylate content in the polymer. This suggests that the rate of the propagation component of the degradation process decreases, and therefore, the overall stability of the polymer increases with increasing butyl acrylate incorporation. This is also reflected in the composite plot of degradation versus temperature for the series of VDC/BA copolymers shown in Fig. 4.

A more quantitative reflection of this phenomenon is provided by the degradation rate constants contained in Table 4. With the exception of the initial

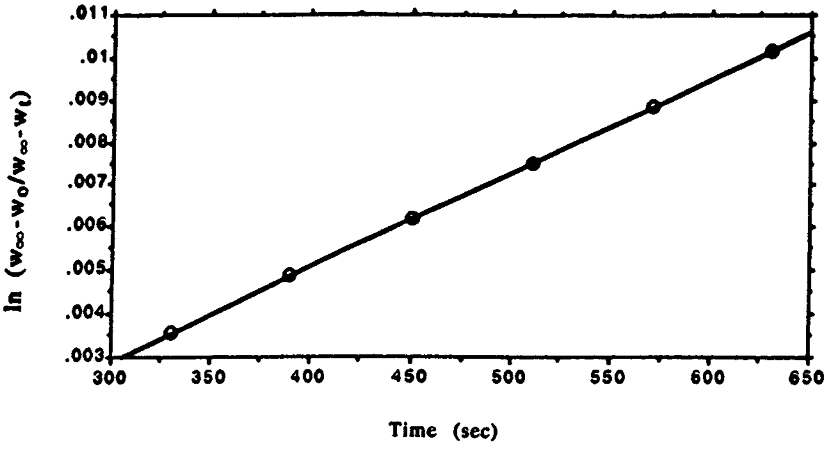


Fig. 2. Initiation rate constant (k_i) for the thermal degradation of a vinylidene chloride/butyl acrylate (20 wt.%) copolymer at 180°C.

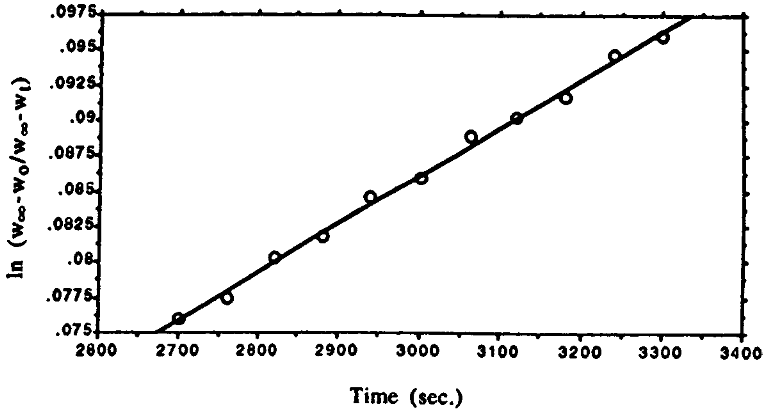
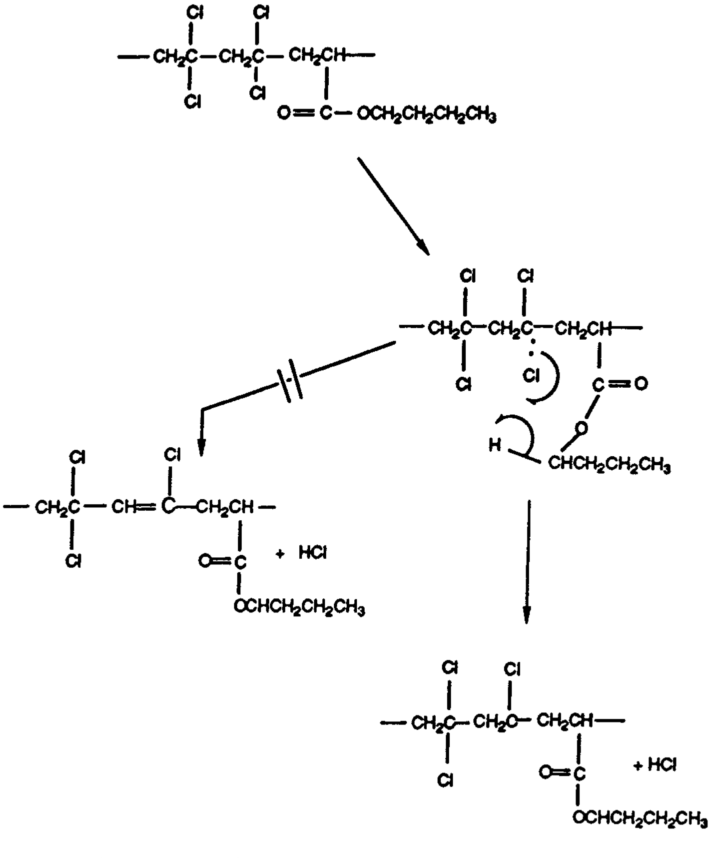


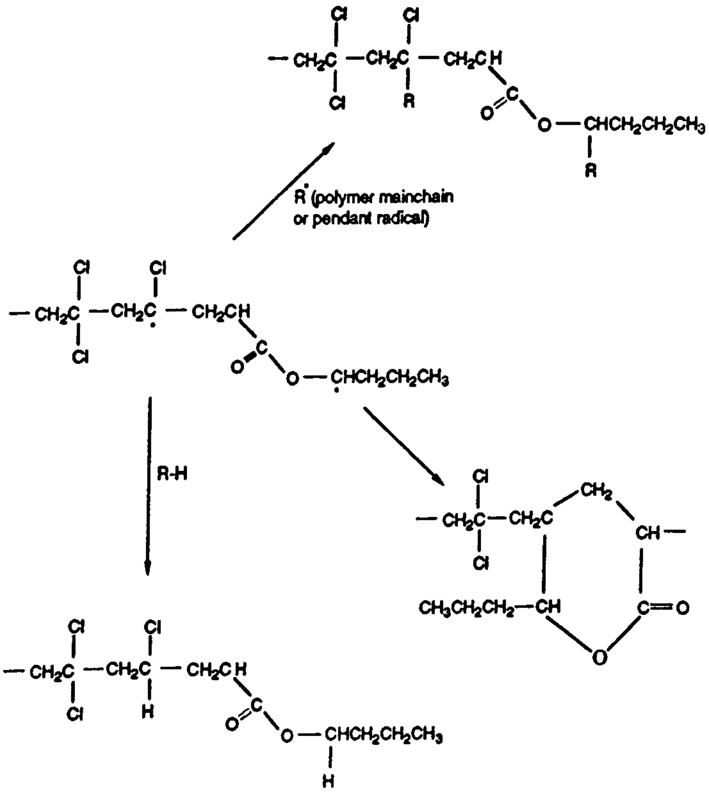
Fig. 3. Propagation rate constant (k_p) for the thermal degradation of a vinylidene chloride/butyl acrylate (20 wt.%) copolymer at 180°C.

comonomer loading, initiation of degradation is little impacted by the incorporation of increasing amounts of butyl acrylate into the polymer (see Fig. 5).

However, the presence of butyl acrylate along the polymer main chain suppresses the rate of propagation of the dehydrochlorination; an effect which becomes greater with an increasing amount of butyl acrylate



Scheme 2. Possible mode of stabilization of vinylidene chloride copolymers containing pendant butyl ester groups.



Scheme 3. Possible fates of radicals generated by butyl ester side chain scavenging of chlorine atoms formed during the degradative dehydrochlorination of vinylidene chloride/butyl acrylate copolymers.

incorporated into the polymer (Fig. 6). The greater stability of the polymer containing a higher percentage of acrylate is probably reflective of the decreasing size of the VDC sequences in the polymer, that is, chain-stopping (termination of the dehydrochlorination reaction) becomes more important as the length of the VDC sequences decreases because of the increasing level of acrylate incorporated into the polymer [8]. The increased stability of the copolymers containing higher levels of butyl acrylate would seem to be of

Table 3
Degradation temperatures for vinylidene chloride/butyl acrylate copolymers

Butyl acrylate (wt.%)[a]	Onset temperature for degradation (°C)[b]	Temperature of max. degradation (°C)[c]
0	206	240.9
4	201	240.0
8	203	241.9
12	200	242.7
18	200	244.1
20	202	246.1

[a] Weight percent of monomer loaded.

[b] Extrapolated onset temperature determined from the derivative plot of weight loss versus temperature.

[c] Maximum in the derivative plot of weight loss versus temperature.

Table 4
Rate constants for the thermal degradation of vinylidene chloride/butyl acrylate copolymers at 180°C

Butyl acrylate (wt.%)[a]	$k_i \times 10^5$ (s^{-1})[b]	$k_p \times 10^5$ (s^{-1})[b]
0	3.20±0.09	8.75±0.14
4	4.48±0.004	8.34±0.28
8	2.83±0.25	6.73±0.01
12	2.76±0.03	5.35±0.18
18	2.45±0.25	4.08±0.05
20	2.21±0.005	3.74±0.33

[a] Weight percent of monomer loaded.

[b] Averages of at least two determinations.

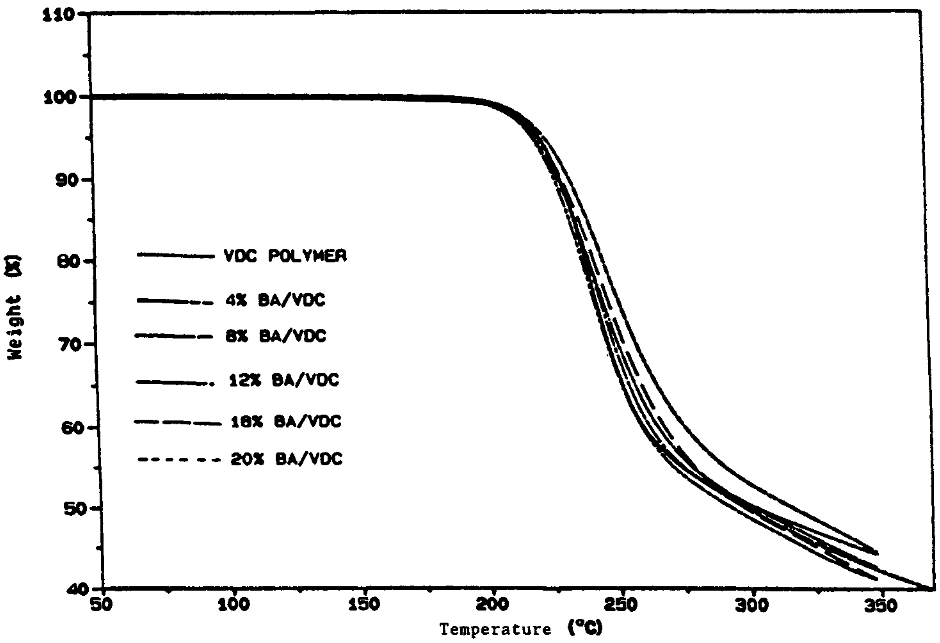


Fig. 4. Thermal degradation of vinylidene chloride/butyl acrylate copolymers containing varying amounts of butyl acrylate.

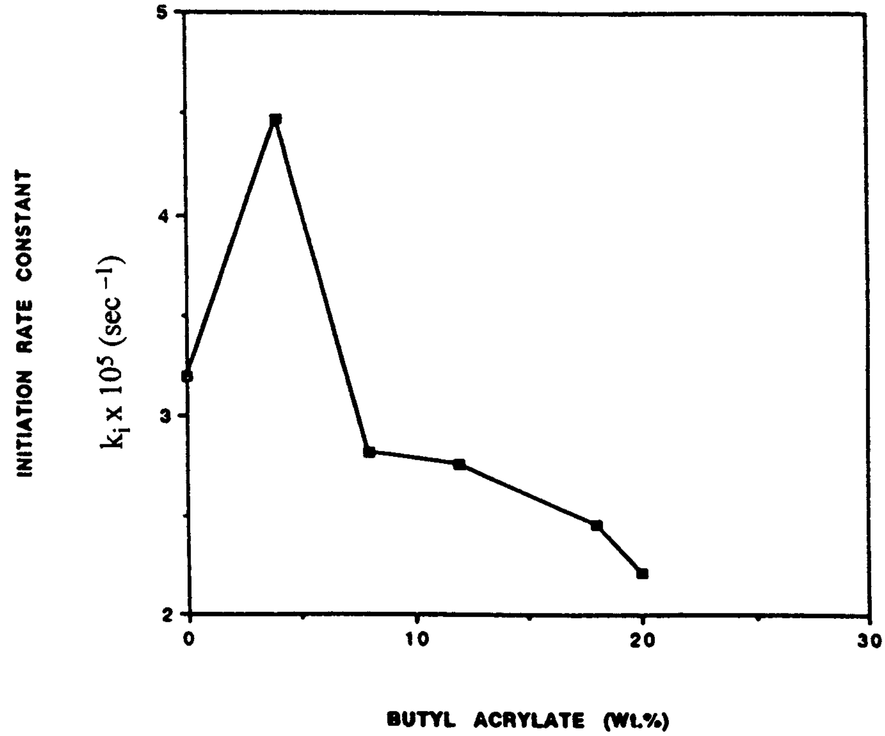


Fig. 5. Initiation rate constants for the thermal degradation of vinylidene chloride/butyl acrylate copolymer as a function of the level of butyl acrylate loading.

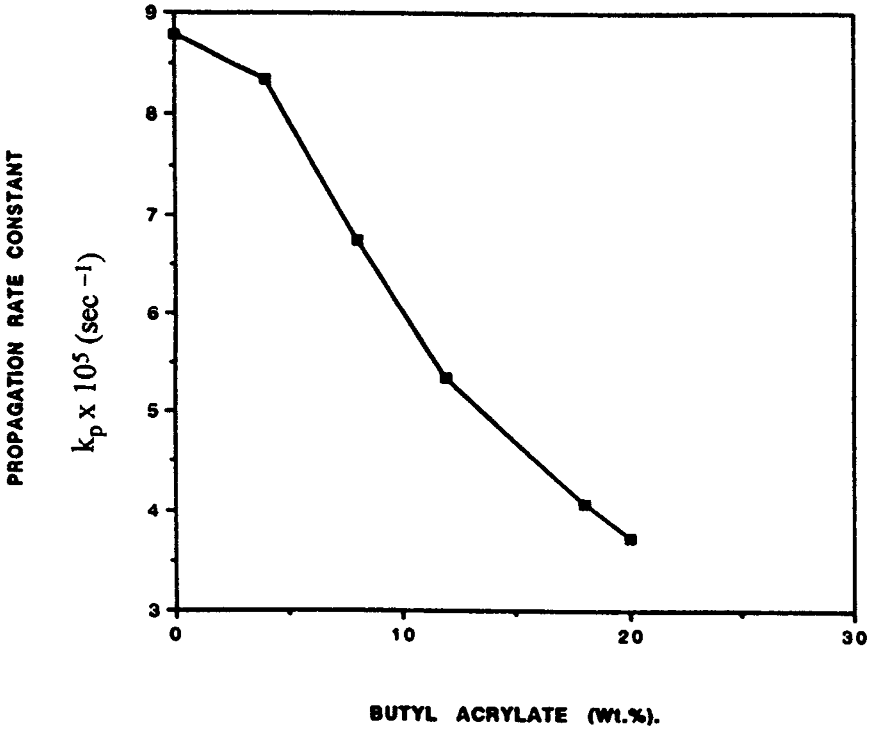


Fig. 6. Propagation rate constants for the thermal degradation of vinylidene chloride/butyl acrylate copolymer as a function of the level of butyl acrylate loading.

insufficient magnitude to reflect significant chlorine atom scavenging by the relatively short (four carbon atoms) alkyl side chain.

4. Conclusions

The thermal stability of vinylidene chloride/butyl acrylate copolymers increases as the level of butyl acrylate present increases. The initiation of degradation is largely unaffected by increasing butyl acrylate content of the copolymers. However, increasing amounts of butyl acrylate in the copolymers does suppress the rate of propagation of the degradation process. This is most likely due to chain-stopping of the degradative dehydrochlorination process as the length of the vinylidene chloride sequences in the copolymer decreases as a consequence of higher levels of acrylate in the polymer.

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