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Studies in Vinyl Polymerization. Reinitiation by Allyl Chloride Transfer Radicals in the Polymerization of Vinyl Acetate

Ebhodaghe F. Okieimen^a; Arthur Jideonwo^a

^a Department of Chemistry, University of Benin, Benin City, Nigeria

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NOTE

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EBHODAGHE F. OKIEIMEN and ARTHUR JIDEONWO

Department of Chemistry
University of Benin
Benin City, Nigeria

ABSTRACT

The kinetics of vinyl acetate polymerization in the presence of allyl chloride were studied by a dilatometric method. The retardation of the rate of polymerization was explained in terms of degradative chain transfer to allyl chloride. Analysis of the polymerization rate data indicates that a relatively large proportion of the allyl chloride transfer radicals is reactive toward initiation.

INTRODUCTION

It is generally well recognized that in the presence of transfer agents, the rate of free-radical polymerization of vinyl monomers is greatly reduced due to the formation, by transfer reactions, of resonance-stabilized transfer radicals. Thus, in the kinetic analysis of polymerization rate data involving transfer agents, termination by the transfer radicals of the growing polymer chains is considered the main reaction of the transfer radicals. However, the results from copolymerization studies of allyl compounds with vinyl monomers [1-4] indicate that a large proportion of the allyl molecules may be incor-

porated in the polymer chain by way of initiation by the allyl transfer molecules. This note examines the contribution of allyl chloride transfer radicals to the overall initiation process in the polymerization of vinyl acetate in dichloroethane.

EXPERIMENTAL

Commercial vinyl acetate from BDH Ltd. was purified as described previously [5]. Benzoyl peroxide from BDH Ltd. was purified by precipitation from acetone solution using methanol. Analytical grade 1,2-dichloroethane was used without further purification. Allyl chloride from BDH Ltd. was purified as described previously [3]. Polymerizations were carried out in dilatometers of about 20 cm³ at 60°C in a thermostatic bath. The polymerization was followed with a cathetometer, and after 5% conversion the reaction was quenched in liquid nitrogen.

RESULTS AND DISCUSSION

The rate of vinyl acetate polymerization in the presence of various amounts of allyl chloride (Fig. 1) shows that, as the amount of allyl chloride increased from 10% (i.e., [AC]/[VA] = 0.10) to 70%, the relative rate of vinyl acetate polymerization, R_p/R_{p0} (the ratio of the rates of polymerization in the presence and absence of allyl chloride) dropped by 50%. This retardation can be explained in terms of degradative chain transfer to allyl chloride.

Deb [6] worked out detailed relationships for determining the effects of chain transfer and primary radical termination acting simultaneously or sequentially on vinyl polymerization. When chain transfer is predominant, the relationship

$$\frac{[I][M]^2}{R_p^2} = \frac{k_t}{2fk_d k_p^2} + \frac{C_s[SH]k_{tA}}{fk_d k_{iA} k_p [M]} \left\{ 1 + \frac{k_{tA} R_p}{k_{iA} k_p [M]^2} \right\} \quad (1)$$

allows the characteristic constant of degradative transfer, $C_d = k_{tA}/(k_{iA} k_p)$ to be evaluated from the plot of $[I][M]^2/R_p^2$ against $R_p/[M]^2$.

Here k_{tA} and k_{iA} are the rate constants for the termination of growing polymer chain by the transfer radical and for the addition of monomer to the transfer radicals. Such a plot for our data $C_d = 1.43 \times 10^7$ mol·L⁻¹·s⁻¹ for allyl chloride.

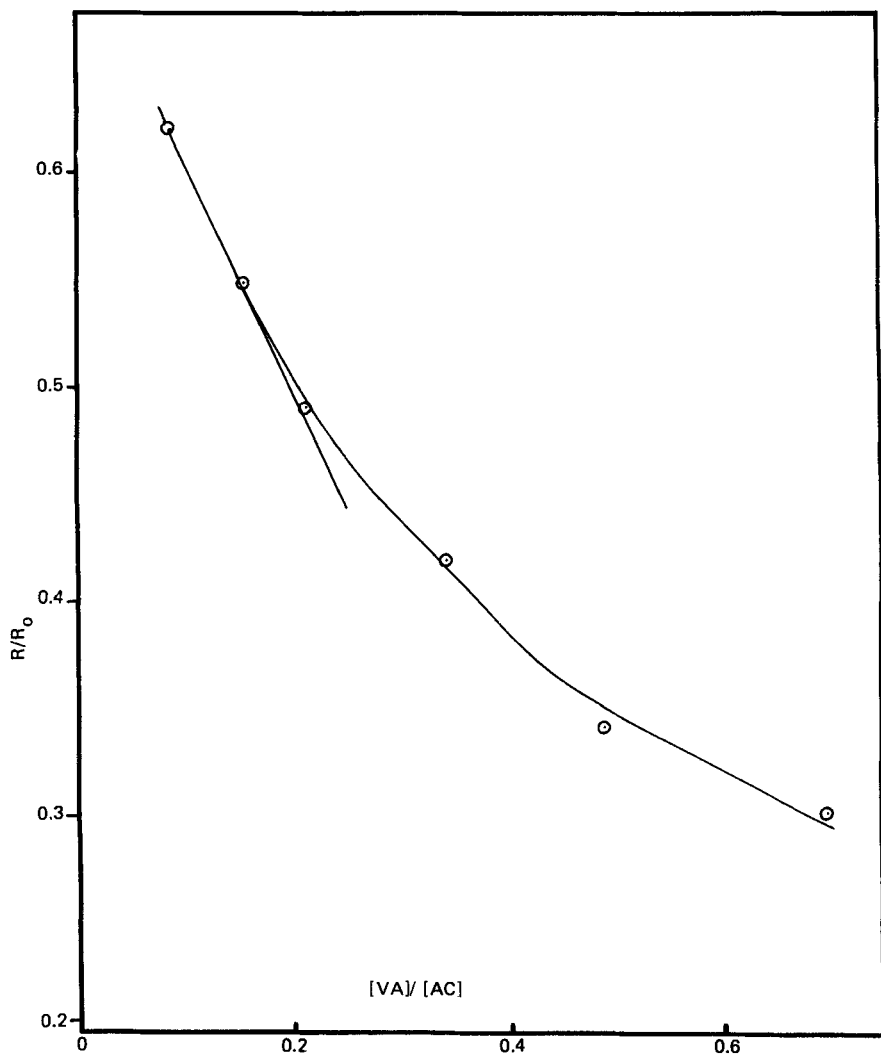


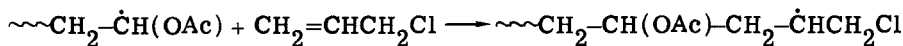
FIG. 1. Variation of the rate of vinyl acetate polymerization with allyl chloride concentration.

The significance of C_d can be assessed from the ratio of the rate of termination of growing polymer chain by the transfer radical, R_{tA} , to the rate of initiation by the transfer radicals, R_{iA} :

$$R_{tA}/R_{iA} = k_{tA}R_p/k_{iA}k_p[M]^2 \quad (2)$$

By substituting the value of $k_{tA}/k_{iA}k_p$ and the polymerization data from this study in Eq. 2, R_{tA}/R_{iA} values between 0.91 and 0.50 were obtained, comparable to those between 0.82 and 0.48 reported for the vinyl chloride-allyl chloride system [4].

The analysis of the data from this study assumes that 1) the observed retardation of polymerization was due only to degradative chain transfer to allyl chloride, and 2) all the transfer radicals are consumed in termination and initiation reactions. Polymerization of vinyl acetate in the presence of allyl chloride would lead to the incorporation of allyl chloride molecules in the polymer chain:



Growing polymer chains with an allyl chloride terminal molecule would react less readily with either the monomer or with themselves. Such retardation by copolymerization [7, 8], which is not distinguishable from degradative chain transfer by kinetic data, would be expected to make significant contribution to the observed retardation of polymerization. Furthermore, abstraction of hydrogen from the solvent and/or from the monomer by the transfer radicals and dimerization of the transfer radicals could compete with the termination and initiation reactions and could further complicate the kinetic relationship in Eq. 1. Thus, although the results from this study indicate that allyl chloride transfer radicals are reactive toward initiation, evidence from molecular weight data and the analysis of the polymer samples for combined allyl chloride molecules would be required for a complete assessment of the contribution of reinitiation by the transfer radicals to the overall initiation process.

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