PHOTOPOLYMERIZATION MECHANISMS OF VINYL COMPOUNDS:
ROLE OF THE TRIPLET STATE OF THE MONOMER IN INITIATION

V. A. Krongauz

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It is concluded that the triplet state of the monomer plays a part in the initiation of photopolymerization of methyl methacrylate; this has been deduced from the kinetics of the sensitized trans-cis isomerization of the stilbene in response to light absorbed by the ester and also from the polymerization kinetics of the ester in the presence of stilbene. Some notable kinetic features of this photopolymerization are reported.

I have shown [1] that light of wavelength 254 μm causes sensitized trans-cis isomerization of trans-stilbene dissolved in benzene, although only the solvent absorbs this light. The isomerization is caused by triplet-triplet energy transfer from benzene to stilbene, the singlet excited states of benzene not being involved. The quantum yield shows a concentration effect that gives lower limits for the yield of the triplet state (GT ≤ 0.25) and the lifetime (τt ≤ 10⁻⁶ sec).

This sensitized isomerization provides a convenient way of examining triplet states produced by light in organic liquids if sensitized fluorescence is difficult to detect on account of the low steady-state concentration of the triplet state. The effect is used here to detect the triplet state produced in a vinyl monomer.

It is supposed [2] that the initiating radicals in photopolymerization are produced by unimolecular conversion of the primary excited molecules. This process was later [3] considered as production of the triplet state, in accordance with Terenin's [4] views.

Norrish et al. [5, 6] have shown that styrene polymerizes when it acts as solvent for anthracene and is exposed to light absorbed by the latter. Flash photolysis has shown that styrene deactivates the triplet state of anthracene, and it has been concluded that this state initiates the polymerization of the styrene. However, Norrish's results do not rule out an effect from excited singlet molecules of anthracene.

I have compared the sensitized isomerization of stilbene in methyl methacrylate with the photopolymerization kinetics of the ester in the presence of stilbene in order to elucidate the nature of the initiating particles.

METHODS

The dilatometer method was applied to the photopolymerization. The mean molecular weight of the products was found from \[ n = 4.8 \times 10^{-5} \] (1.9 \( M_n \)) \[ \times \] in which \( n \) is the characteristic viscosity in chloroform and \( M_n \) is the mean molecular weight. The quantum yield for the isomerization was deduced from the optical density in the early stages [1]. The two stilbenes differ considerably in ultraviolet absorption (Fig. 1), so they can be assayed separately. The optical densities of solutions in methyl methacrylate were measured at 300-330 μm, where the solvent is reasonably transparent.

The carefully purified monomer and the solutions were degassed under vacuum before use.

The light source was a PRK-2 mercury lamp, the 253.7-265.2 μm lines being isolated by a combination of a chlorine-bromine filter with an aqueous \( \text{NiSO}_4 - \text{CoSO}_4 \), the 303-313 μm lines by a combination of \( \text{NiSO}_4 \) and \( \text{K}_2\text{CrO}_4 \) solutions. Bands of λ > 400 μm were isolated with an SS-14 glass filter. The actinometer was iron oxalate [7, 8].

NATURE OF INITIATING PARTICLES

Figure 2 shows the quantum yield \( γ \) for the trans-cis isomerization as a function of stilbene concentration \( c \) for the 253.7-265.2 μm region at 30°C; the rise in \( γ \) with \( c \) is rapid up to about 10⁻⁴ M (as for benzene solutions), a constant limit occurring above 4 × 10⁻⁴ M.

The mean absorption coefficient \( ε_m \) of the ester in cyclohexane at 254-265 μm is about 50 liter/mole·cm; trans-stilbene has a coefficient \( ε_x \) of about 3 × 10⁻⁴ in this region, so it absorbs about 6.5 × 10⁻⁴ of the light in 10⁻⁴ M solution if we use the \( ε_x/ε_m \) for dilute solutions (M and x are the concentrations of the components). The \( γ \) for light acting directly on stilbene is ≤ 1 (0.48 for trans-stilbene in the ester at 303-313 μm), so the maximal \( γ \) for the light absorbed by the whole system is about 6.5 × 10⁻⁴ if there is no
migration of the primary energy. This is well below the measured $4.5 \times 10^{-3}$. Moreover, $\gamma$ should be proportional to $c$ if direct action on the stilbene is the cause. The isomerization of trans-stilbene is thus caused by the solvent, and it has been shown [1] that only triplet-triplet migration can account for this. The Stern-Volmer equation applies to $\gamma$ below $10^{-4}$ M, and this implies that transfer competes with deactivation of the monomer triplet state [1]. All the triplet molecules perform the transfer before deactivation above $10^{-4}$ M. The minimal $\tau$ and $\gamma_t$ are respectively $10^{-3}$ sec and $4.5 \times 10^{-3}$.

Fig. 2. Effects of concentration in methyl methacrylate for quantum yields of isomerizations of stilbenes: 1) trans-cis ($\gamma_t$), and 2) cis-trans ($\gamma_t$); $\lambda$ of 254-265 mum.

Comparison was made with the effects on polymerization induced by the radicals from phenylazotriphenylmethane (0.01 M), which at $30^\circ$C is decomposed by light of $\lambda > 400$ mum (the absorption peak lies at about 420 mum), where the stilbene and ester have negligible absorption. The addition of $2 \times 10^{-4}$ M of trans-stilbene does not affect the polymerization rate; the initial rate is also proportional to the square root of the intensity, which shows that the stilbene produces no inhibition, whereas $2 \times 10^{-4}$ M of cis-stilbene reduces the rate by 28% (as in photopolymerization). This effect cannot be related to specific features of the initiation; it arises from interaction with the growing polymer radicals (this is demonstrated in part 2 of the next section).

A similar comparison was made at $60^\circ$C, the initiator being azoisobutyryldicyanide (thermal decomposition). Trans-stilbene did not affect the polymerization in the dark but sharply reduced the rate of photopolymerization.

Trans-stilbene thus deactivates the triplet state of the ester and so inhibits photopolymerization; but it does not affect polymerization produced by initiators. This demonstrates the role of the triplet state.

**ASPECTS OF PHOTOPOLYMERIZATION**

The following features are of interest.

1. The quantum yield $\beta$ for initiation at 254-265 mum is given by

$$V_0 = \frac{k_p}{k_0} \frac{M}{\beta} \lambda^{1/2} I$$

in which $V_0$ is the polymerization rate of the pure monomer, $k_p$ and $k_0$ are the rate constants for chain production and termination, and $I$ is absorbed light intensity (einstein/liter-sec). Then $\beta = (1 \pm 0.2) \times 10^{-2}$ if $k_p/k_0^{1/2} = 0.05$ [8] and $M = 3.3$ mole/liter. This $\beta$ is about a fifth of the minimal $\gamma_t$ as found from the isomerization of stilbene; at least four out of every five triplet molecules are deactivated without initiating polymerization.

Bagdasar'yan's [3] results would indicate that this low $\beta$ is related to concentration quenching; but fivefold dilution with ethyl acetate produced very little increase in $\beta$.

Also, $\beta$ and $\gamma$ are independent of the intensity, which shows that uneven absorption in the cell does not produce secondary interactions (deactivation) of triplet states [1].

We may say that the triplet states decay spontaneously.

There is no change in $\beta$ up to $60^\circ$C, but it does increase to about 0.1 when light at 303-315 mum is used; this agrees with Bagdasar'yan's results [3].