Kinetic and Mechanistic Studies of Photopolymerizations of Acrylates in the Presence of Iniferters

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ABSTRACT: In this particular study, the reaction mechanisms of bulk polymerization of acrylates in the presence of tetraethylthiuram disulfide (TED) are investigated using hexyl acrylate as a model acrylate. TED's presence impacts the termination mechanisms of the acrylate polymerization by two pathways: (1) dissociation of TED to generate dithiocarbamate radicals, which could terminate the acrylic radicals, and (2) chain transfer to TED. The impact of TED concentration as well as the initiation rate on the hexyl acrylate polymerization rate was investigated for polymerizations initiated by both UV and visible light. It was observed that for the polymerizations initiated by UV light, the initial polymerization rate (averaged between 5 and 20% conversion) scaled with the initiation rate by a power of 0.86 ± 0.02 at various concentrations of TED, and a power of 0.45 ± 0.05 for polymerizations in the absence of TED. The initial polymerization rate exhibited a near inverse-linear relationship with the concentration of TED, with the order of dependence ranging from −0.96 ± 0.13 to −1.00 ± 0.14. Thus, it was found that chain transfer to TED appears to contribute significantly to the termination mechanisms in the polymerization of acrylates. It was observed that TED does not exhibit any absorbance in the visible range (400−500 nm), and hence, the dissociation of TED was eliminated in the polymerizations conducted by visible light. For these polymerizations initiated by visible light, the initial polymerization rate scaled with the initiation rate by a power of 0.84 ± 0.04 to 0.95 ± 0.05 at various TED concentrations ranging from 0.1 to 0.5 wt %. It was also observed that at a light intensity of 25 mW/cm^2, the log−log plot of the initial polymerization rate as a function of TED concentration exhibited a slope of −1.19 ± 0.03. Thus, the dependence of polymerization rate on the TED concentration was observed to be greater than the expected inverse-linear relationship because of the dependence of the termination kinetic constant on the concentration of TED. Furthermore, it was shown that chain-transfer to TED is the dominant mechanism relative to the dissociation of TED to generate dithiocarbamate radicals, and it appears to contribute significantly to the termination reactions for both polymerizations.

Introduction

"Living" radical polymerizations using iniferters were first conducted by Otsu et al.[1,2] as a means for synthesizing block copolymers in the presence of compounds such as XDT (*p*-xylylene bis(*N*,*N*-diethyldithiocarbamate) and benzyl dithiocarbamate. "Living" radical polymerizations are presently used for various applications such as producing block copolymers, polymers of low polydispersity, and surface modification of fabricated device substrates.[1,3−10] To advance the applications of these iniferter polymerizations,[11−14] it is essential to develop an increased understanding of the polymerization reaction mechanisms in the presence of iniferters. Hence, several researchers have previously investigated the mechanisms of iniferter polymerizations.[15−18] The use of DMPA (2,2-dimethoxy-2-phenylacetophenone) in combination with TED (tetraethylthiuram disulfide) could imitate asymmetric iniferters like XDT[14] and has been used as an alternative to XDT for living radical polymerizations.[3,14,19,20] Hence, this particular study focuses on elucidating the polymerization reaction mechanisms of acrylates in the presence of TED to advance the applications and understanding of iniferter polymerizations.

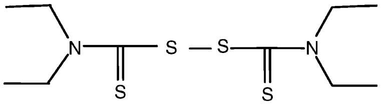

Figure 1. Structure of tetraethylthiuram disulfide (TED).

The reaction mechanism (see Figure 1) consists of initiation, propagation, and termination reactions. In the presence of UV light, TED could either absorb the light to dissociate or chain transfer to the propagating acrylic radical to generate dithiocarbamate radicals. Since the dithiocarbamate radical does not initiate any significant polymerization itself,[21,22] initiation primarily proceeds through the conventional photoinitiator DMPA. The propagation reaction primarily takes place through the carbon radical as the dithiocarbamate radical is stable and relatively unreactive to propagation along acrylic double bonds.[21,22] The termination reaction has three possible pathways: (1) carbon−carbon biradical termination, (2) carbon−dithiocarbamate (DTC) radical termination,[23,24] and (3) chain transfer to TED. In contrast to the acrylates studied here, Kannurpatti et al.[15,16] investigated the XDT initiated polymerizations of methacrylates in the presence of TED and demonstrated that both carbon−carbon biradical termination and carbon−dithiocarbamyl radical termination take place in those systems. Lovell et al.[14] have investigated the DMPA-initiated polymerizations of TEGDMA in the presence of TED and demonstrated the mechanism of termination to be dependent on the ratio of the photoinitiator concentration to TED concentration, with the termination via DTC radicals becoming more prominent at higher concentrations of TED.

This work specifically focuses on characterizing the dependence of the kinetic behavior on the concentration of TED,

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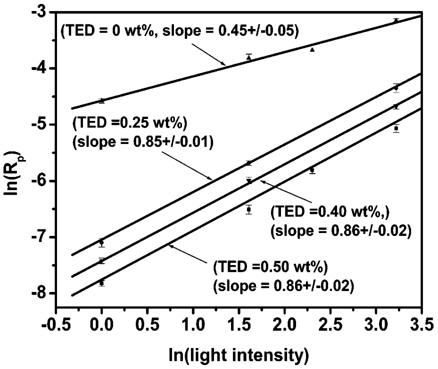

Figure 2. Natural log of the average polymerization rate, ln(R_p), of hexyl acrylate as a function of the natural log of the light intensity at various TED concentrations. Polymerization conditions: initiator concentration = 0.5 wt % DMPA; room temperature. The average polymerization rates have been obtained from the slope of the conversion−time curve in the range from 5 to 20% conversion.

initiating light intensity and wavelength of irradiation. From these polymerization studies initiated by DMPA, conclusions have been presented regarding the polymerization reaction mechanism in the presence of TED.

Experimental Section

Samples were irradiated from an ultraviolet light source (Ultracure 100SS 100 W high pressure. Mercury vapor short-arc lamp, EXFO, Mississaugua, Ontario, Canada) filtered using 320−500 nm and 400−500 nm filters. Conversion vs time data for all monomers was obtained by using real time FTIR[25−27] either by monitoring the C═C stretching vibration at 1630 cm^{-1} or the C═C twisting vibration around 810 cm^{-1}. Samples were laminated between two NaCl crystals achieving approximate film thicknesses of 15−20 μm. The average polymerization rates were obtained from the slope of the conversion−time curves, for a given conversion range.

Ultraviolet−visible spectroscopy (UV−vis) was used to obtain the absorption spectrum of TED with a Perkin-Elmer Lambda 40 UV/vis Systems spectrometer (Perkin-Elmer, Shelton, CT). The excitation source used was a Dolan-Jenner DC-950 DC-Regulated Fiber Optic Illuminator (Lawrence, MA) with a red filter. The photoinitiators used were Irgacure 819 and 2,2-dimethoxy-2-phenylacetophenone (DMPA) purchased from (Ciba Geigy, Hawthorne, NY). The monomer hexyl acrylate and TED were purchased from Aldrich Chemicals (Milwaukee, WI), and hexyl acrylate was deinhibited prior to use by vacuum distillation.

Results and Discussion

The reaction mechanism in the presence of TED was investigated by conducting studies, on the impact of the TED concentration as well as the initiation rate on the polymerization kinetics of the acrylate monomers. Since the initiation rate is directly proportional to the light intensity, the light intensity was varied between 1 and 25 mW/cm^2, to study the effect of initiation rate on the polymerization kinetics at various TED concentrations. Figure 2 is a log−log plot of the average polymerization rate (averaged from 5%−20% conversion) vs light intensity at different concentrations of TED. The slope of the straight line in the absence of TED is 0.45 ± 0.04 in good agreement with the classical square root rate dependence. The slope of the straight line varies from approximately 0.85 ± 0.01 to 0.86 ± 0.02, at various concentrations of TED suggesting near linear dependence of polymerization rate on initiation rate. Furthermore, due to a higher dependence of polymerization kinetics on the initiation rate relative to conventional photopolymerizations, polymerizations in the presence of TED could also enable the creation of steeper polymerization rate gradients. This feature would be advantageous in improving the resolution of the structures formed through photolithography,[3,28,29] i.e., techniques that utilize this polymerization approach.

Reaction Mechanisms in the Presence of TED. In the presence of TED, two reaction mechanisms are possible. First, TED could act as a chain transfer agent and terminate the growing acrylic radical. Second, TED could dissociate to form the dithiocarbamate radicals which can cross-terminate with the propagating acrylic radicals. The equations below represent the reaction mechanisms for both cases.

Case 1: Chain transfer to TED is the dominant mechanism

$$\mathrm{DMPA} \rightarrow \mathrm{R_C}^{\bullet} + \mathrm{R_C}^{\bullet} \tag{1}$$

$$\mathrm{R_C}^{\bullet} + \mathrm{TED} \rightarrow \mathrm{P} \tag{2}$$

Case 2. Cross termination by DTC radicals produced through the cleavage of TED is the dominant mechanism.

$$\mathrm{DMPA} \rightarrow \mathrm{R_C}^{\bullet} + \mathrm{R_C}^{\bullet} \tag{3}$$

$$\mathrm{TED} \overset{h\nu}{\longleftrightarrow} \mathrm{R_S}^{\bullet} + \mathrm{R_S}^{\bullet} \tag{4}$$

$$\mathrm{R_C}^{\bullet} + \mathrm{R_S}^{\bullet} \leftrightarrow \mathrm{P} \tag{5}$$

Performing mass balances on the carbon ($\mathrm{R_C}^{\bullet}$) and thiyl ($\mathrm{R_S}^{\bullet}$) radicals and utilizing pseudo steady state assumptions on the radical concentrations show that the initial polymerization rate is linearly proportional to the initiation rate and inversely proportional to the TED concentration, if chain transfer to TED is the dominant termination mechanism (case 1).[16]

If cross-termination by the DTC radicals generated from the cleavage of TED is the dominant mechanism (case 2), then the polymerization rate would be proportional to the square root of the light intensity and inversely proportional to the square root of the TED concentration.[16]

Figure 3 compares the normalized polymerization kinetics of hexyl acrylate at various TED concentrations where the polymerization time scale is normalized with the dependence on the initiation rate. It can be inferred from Figure 3 that the polymerization kinetics of all systems exhibit significant autoacceleration in the presence of TED. This autoacceleration effect arises from growing polymeric radical chain length which increases the diffusional resistance for termination with TED and suppresses the termination of hexyl acrylate with TED. This autoacceleration effect is not so pronounced in the pure hexyl acrylate system because acrylates exhibit significant amounts of chain-transfer to the polymer backbone,[30,31] which also contributes to the termination mechanisms of hexyl acrylate. However, in the presence of TED, the chain-transfer to TED dominates the termination mechanism, and autoacceleration effects are more pronounced as seen in Figure 3. Furthermore, since an increase in TED concentration is also associated with the decrease in the polymeric radical chain length, it can be expected that after an optimum TED concentration the autoacceleration effects should decrease. For example, it can be observed in Figure 3 that the autoacceleration effects are more pronounced at a TED concentration of 0.25 wt % as compared to 0.5 wt %. Since the polymeric radical chain length is also a function of the initiation conditions (i.e., the initiating light intensity and initiator concentration), the optimum TED concentration for observing increased autoacceleration effects is different for different initiation conditions.

It can also be inferred from Figure 3 that, even though the polymerization rates are similar at lower conversions, for all

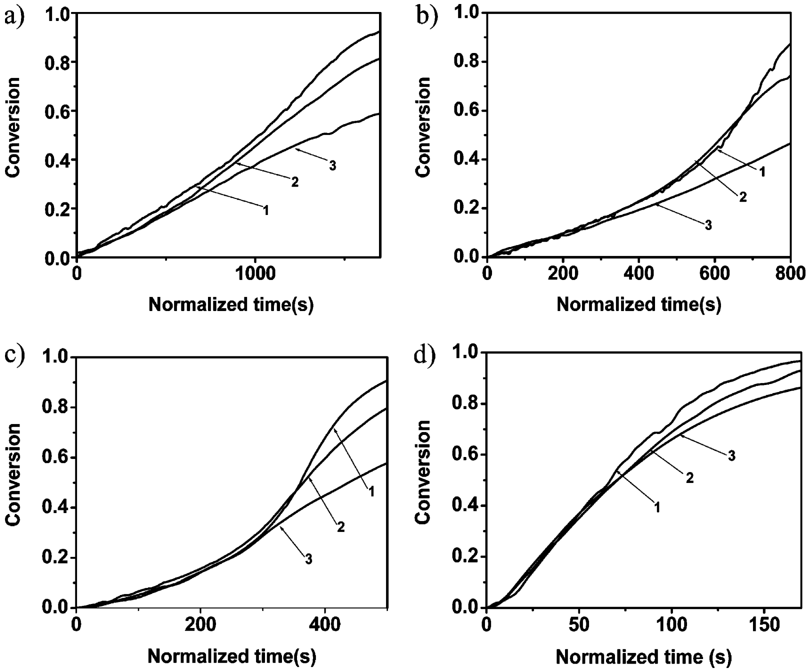

Figure 3. Hexyl acrylate conversion as a function of time normalized by the dependence on the light intensity, α, at different TED concentrations: (a) 0.5 wt % TED, α = 0.86; (b) 0.4 wt % TED, α = 0.86; (c) 0.25 wt % TED, α = 0.85; (d) no TED, α = 0.45. Curves 1−3 represent polymerization at 1, 5, and 25 mW, respectively. Polymerization conditions: initiator concentration = 0.5 wt % DMPA, room temperature. The normalized time is obtained by dividing the time by the light intensity raised to the exponent α.

systems the normalized rate curves at higher extents of conversion exhibit lower polymerization rates with increasing light intensities. This behavior is due to the fact that higher light intensities result in increased radical concentrations and consequently shorter radical chain lengths leading to enhanced mobility. The greater mobility at higher light intensities leads to enhanced termination and suppressed overall polymerization kinetics. Furthermore, it can be inferred from Figure 3 that for systems with only DMPA the normalized conversion curves are similar up to approximately 50% conversion. Upon the addition of 0.25 wt % TED the polymerization kinetics are similar up to only approximately 30% conversion, and upon the addition of 0.5 wt % TED, the polymerization kinetics were similar up to only 22% conversion.

This result is due to the fact that in the presence of TED, the radical concentration scales to a much higher power of the initiation rate. For instance, for the pure hexyl acrylate DMPA system, the initial polymerization rate (averaged from 5% to 20% conversion) scales to the irradiating light intensity with an exponent of 0.45 ± 0.04, whereas in the presence of TED, the exponent is approximately 0.86 ± 0.02. Thus, in the presence of TED, the difference in the radical concentrations would be greater for similar variation in light intensity. Hence, the presence of TED leads to a greater difference in radical concentrations over the same intensity range which leads to a broader distribution of polymer chain lengths over the same light intensity range. Thus, because of the broader distribution of polymer chain lengths,[26,32] the autoacceleration effects observed at each intensity differ, and the normalized rate curves deviate at lower extents of conversion in the presence of TED. However, in the absence of TED, the distribution of chain lengths should also be comparatively narrower and the autoacceleration effects are also less pronounced, causing the normalized rate curves to deviate at higher extents of conversion.

Figure 4 is a log−log plot of the initial polymerization rate vs TED concentrations at different light intensities. The slope of the straight line varies approximately from −0.95 ± 0.13 to −1.00 ± 0.14, at various concentrations of TED, suggesting near-inverse linear dependence of polymerization rate on TED concentration. Furthermore, the dependence on the TED concentration appears to be greater than the dependence on the light intensity. This dependence is because higher TED concentrations reduce the chain length of the growing acrylic radicals and enhance the mobility of the system. The enhanced mobility in the system increases the termination kinetics and further suppresses the polymerization kinetics along with the rate reduction already present as a result of inhibition due to chain transfer to TED. Thus, the effective dependence of termination kinetic constant k_t on the TED concentration is lumped with the idealized inverse-linear dependence on TED to give an overall higher dependence on the TED concentration.

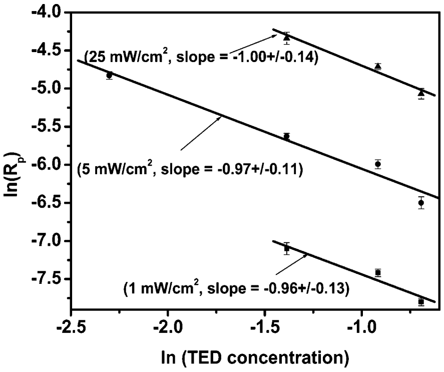

Figure 4. The log of the average polymerization rate, ln(R_p), of hexyl acrylate as a function of the log of the TED concentration at various light intensities. Polymerization conditions: initiator concentration = 0.5 wt % DMPA, room temperature. The polymerization rates have been averaged from 5 to 20% conversion.

Hence, these results have demonstrated that for the acrylate systems the chain-transfer to TED appears to contribute significantly to termination reactions. Furthermore, examining the UV−vis absorption spectrum of TED (Figure 5), we infer that TED exhibits some absorbance in the region of UV irradiation, of 320−500 nm. Hence, some contribution of the

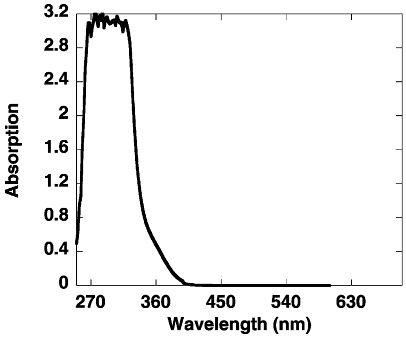

Figure 5. Absorption spectrum of TED. Experiment conditions: wavelength range of irradiation = 250−600 nm; 0.5 wt % in methanol; path length = 1 cm; room temperature.

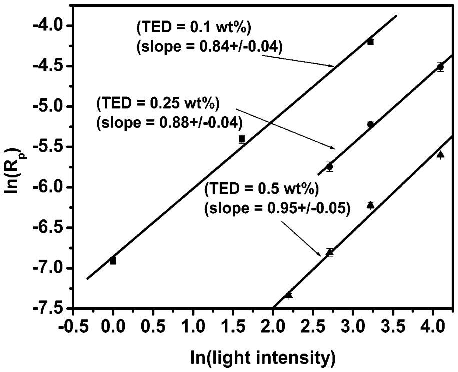

Figure 6. The log of the average polymerization rate, ln(R_p), of hexyl acrylate as a function of the log of the light intensity at various TED concentrations for polymerization initiated by visible light (400−500 nm). Polymerization conditions: initiator concentration = 0.5 wt %; room temperature. The polymerization rates have been averaged from 5 to 20% conversion.

C°−S° cross-termination associated with the dithiocarbamate radicals generated by the dissociation of TED, also cannot be ruled out. Hence, we conducted polymerization studies initiated by visible light, in the presence of Irgacure 891 to eliminate the possible dissociation of TED.

Polymerization Kinetics in the Presence of Visible Light. The visible light intensity was varied from 1 and 60 mW/cm^2, to study the effect of initiation rate on the polymerization kinetics at various TED concentrations. Figure 6 is a log−log plot of the initial polymerization rate vs light intensity at different TED concentrations. The slope of the straight line varies from 0.84 ± 0.04 to 0.95 ± 0.05, at various TED concentrations, indicative of near linear dependence of polymerization rate on initiation rate. Figure 7 shows the normalized polymerization kinetics of hexyl acrylate at various TED concentrations where the polymerization time scale is normalized with the dependence on the initiation rate. It can be inferred from Figure 7 that increasing concentrations of TED result in a more delayed onset of autoacceleration effects, suggesting that at higher TED concentrations there is predominantly higher contribution to the termination kinetics from the chain transfer to TED. This observation is also consistent with the fact that increasing TED concentrations lead to a greater dependence of the polymerization rate on the initiation rate as seen in Figure 6. For instance at 0.1 wt % TED concentration the dependence on the initiation rate is a power of 0.84 ± 0.04, whereas for 0.5 wt % TED concentration this value is 0.95 ± 0.05.

Figure 8 shows a log−log plot of the initial polymerization rate vs TED concentrations at a light intensity of 25 mW/cm^2. The slope of the straight line is −1.19 ± 0.03, which is greater than the expected slope of −1 that would be observed, if chain

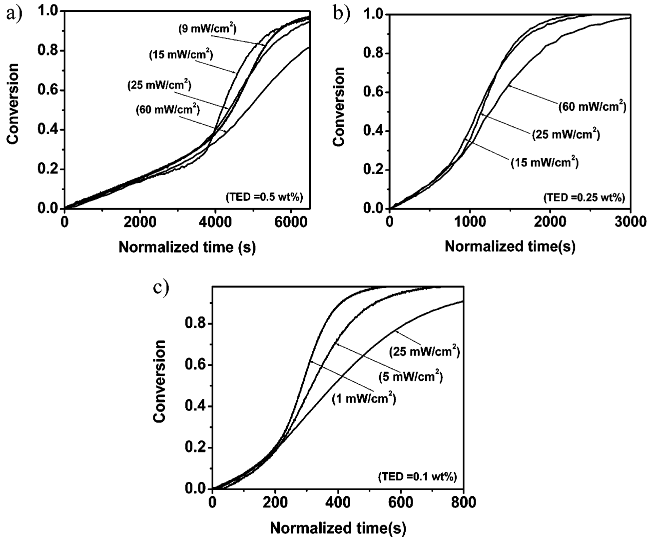

Figure 7. Hexyl acrylate conversion as a function of time normalized by the dependence on the light intensity, α, at different TED concentrations: (a) 0.5 wt % TED, α = 0.95; (b) 0.25 wt % TED, α = 0.88; (c) 0.1 wt % TED, α = 0.84. Polymerization conditions: initiator concentration = 0.5 wt %; room temperature. The normalized time is obtained by dividing the time by the light intensity raised to the exponent α.

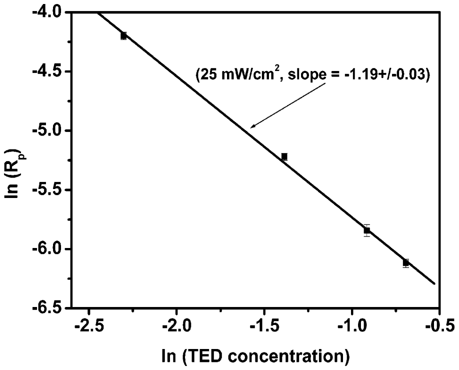

Figure 8. The log of the average polymerization rate, ln(R_p), of hexyl acrylate as a function of the log of the TED concentration at various light intensities for polymerizations of hexyl acrylate initiated by visible light. Polymerization conditions: initiator concentration = 0.5 wt %; room temperature. The polymerization rates have been averaged between 5 and 20% conversion.

transfer to TED were the only termination path. As inferred before, the addition of TED reduces the chain length of the growing acrylic radicals and enhances the mobility of the system to enhance the termination kinetics. Thus, the addition of TED also reduces the polymerization rate by enhancing the termination kinetic constant, resulting in observed scaling greater than the expected inverse-linear relationship as was seen in the UV initiated polymerizations.

Upon comparing the UV initiated and visible light initiated systems it can be inferred that at the same TED concentration, the polymerization rate scales to a higher power of initiation rate for the visible light initiated systems. For example, at a TED concentration of 0.5 wt %, the initial polymerization rate scales to a power of 0.86 ± 0.02 for the UV initiated systems and 0.95 ± 0.05 for the visible initiated systems. These results suggest that for the UV initiated polymerizations, there is some contribution from the termination with the dithiocarbamate radicals generated by the cleavage of TED. For the visible light initiated systems, the dissociation of TED was eliminated and this results in a slightly higher dependence of the polymerization rate on the initiation rate. However, chain transfer to TED was observed to contribute significantly to both polymerizations. Thus, it can be expected that chain-transfer to TED is the dominant mechanism of termination for both mono and multivinyl acrylates. Similar investigation of the monomer kinetics enables the determination of the primary mode of termination for methacrylates and other vinyl monomers.

Conclusions

In this manuscript, polymerizations in the presence of TED have been studied using hexyl acrylate as a model acrylate. The dependence of the kinetic behavior on the TED concentration, the light intensity, and the irradiation wavelength has been characterized. Both the UV initiated and visible light initiated polymerizations depicted near-linear dependence of the initial polymerization rates on the light intensity and near-inverse linear dependence of the polymerization rate on TED concentration. The dependence of initial polymerization rate on the light intensity was greater for the visible light initiated polymerizations as compared to the UV initiated polymerizations due to elimination of the contribution of the carbon-dithiocarbamate radical termination due to the dissociation of TED. The results also suggested that chain transfer to TED is the dominant mechanism of termination relative to the termination by the dithiocarbamate radicals generated by the dissociation of TED, and it appears to contribute significantly to termination reactions in both types of polymerization.

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