Tetrahedron Letters No. 30, pp. 2181-2188, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE SPONTANEOUS COPOLYMERIZATION OF BICYCLO [2.2.1] HEPT-2-ENE AND SULFUR DIOXIDE[1]. EVIDENCE FOR PROPAGATION BY BI-RADICAL COUPLING.

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(Received 4 October 1963; in revised form 21 October 1963)

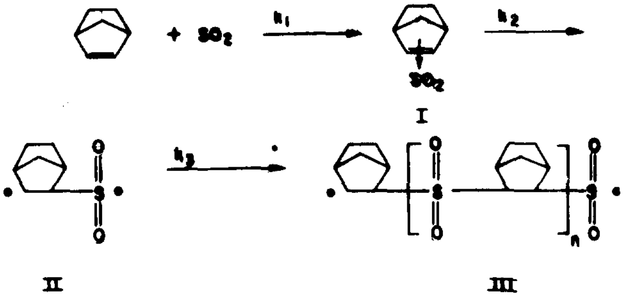
While investigating the polymerization behavior of compounds containing the bicyclo [2.2.1] heptane nucleus[2] we attempted to repeat an experiment first done by Caldwell and Hill[3] in which they reported the copolymerization of bicyclo [2.2.1] hept-2-ene and sulfur dioxide to occur in the presence of a free-radical catalyst over the course of several hours.

Quite surprisingly, upon mixing a toluene solution of very pure bicyclo[2.2.1]hept-2-ene with liquid sulfur dioxide at -20°C, in the absence of initiator an extremely rapid reaction ensued which almost instantly blew a white solid out of the flask.

Upon characterization, by solution viscosity and elemental analysis, the solid was found to be a high molecular weight copolymer containing equimolar amounts of sulfur dioxide and bicyclo-[2.2.1]hept-2-ene.

To establish that oxygen was not taking part in the initiation reaction, triply distilled and degassed monomers were mixed together under high vacuum. High polymer was again formed.

We should now like to report preliminary data which are consistent with a novel polymerization mechanism which may be represented, thus:



Inherent in this mechanism is the fact that in an uncontaminated system little, if any, termination reactions leading to "dead" polymers chains can occur. Thus, "living" free-radical polymers result. This scheme involves the reaction of bicyclo-[2.2.1]hept-2-ene and sulfur dioxide to form a complex (k_1), which rearranges to a diradical (k_2), which then propagates by coupling (k_3).

Identical experiments were set up whereby equal weights of bicyclo [2.2.1]hept-2-ene (carefully purified via fractionation and alkali extraction) and sulfur dioxide (Matheson, C. P. Grade), at a total concentration of 15 wt.% in cyclohexanone, were allowed to polymerize at 0°C for varying lengths of time; after which the reaction was stopped by flooding with hydroquinone dissolved in cyclohexanone. Time zero was taken as the point of addition of liquid sulfur dioxide to the olefin-cyclohexanone solution; and the reaction time was taken as the time elapsed at the addition of the hydroquinone.

The data obtained from these experiments are shown in Fig. 1. From these data it can be seen that after ten seconds of reaction, polymer having a reduced viscosity (2 g/l in cyclohexanone at 30°C) of about 0.3 is formed and that conversion to polymer is around 65%. After about 40 seconds reduced viscosity is 1.8 but conversion to polymer has remained essentially constant. Note that after about one minute both reduced viscosity (about 2.0) and conversion remain constant. If equal molar concentrations of reactants are used in similar experiments, conversions well over 90% result at points along a similar curve. These data, of course, are much different than those obtained during normal free radical, addition polymerizations and are, indeed, indicative of the condensation of a bifunctional species, which, in this case we postulate to be a biradical. Polymer molecular weights are only limited by diffusion.

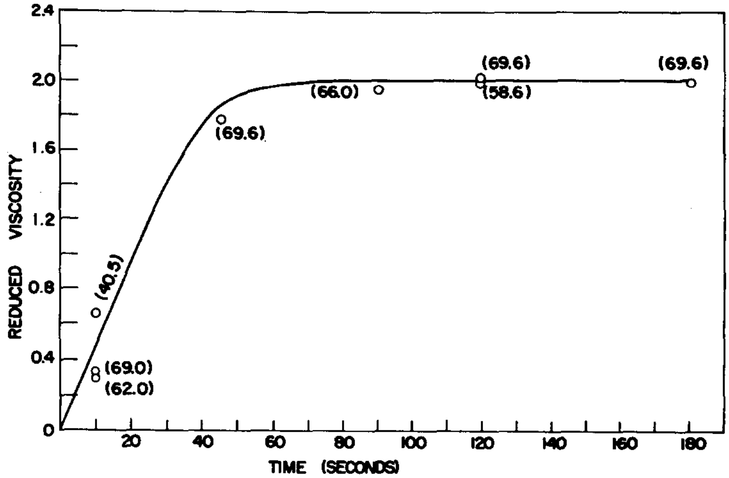


FIGURE 1

The Copolymerization of Bicyclo [2.2.1] hept-2-ene and Sulfur Dioxide at 0°C in Cyclohexanone. (The figures in parentheses are conversion to polymer at given times.)

It is also indicative of this mechanism that when, at any point along this curve, the polymerizing bicyclo [2.2.1] hept-2-ene sulfur dioxide solution is added to ethyl acrylate, immediate (and normal) polymerization of the ethyl acrylate occurs, and leads to polymers whose physical properties are consistent with those expected from a block polymer. These phenomena will be reported in more detail in the future.

It is interesting that polymerization of bicyclo [2.2.1] hept-2-ene and sulfur dioxide will not occur if both reactants, at room temperature, are in the vapor state; but occurs extremely readily if the bicyclo [2.2.1]hept-2-ene is solid (or liquid) while the SO_2 is gaseous. Perhaps this is because the complex (k_1) will not form in the vapor phase.

Preliminary electron paramagnetic resonance (EPR) studies of the bulk copolymerization of bicycloheptene (BCH) with SO_2 also support the proposed mechanism. While EPR signals could not be detected in samples of BCH or SO_2 alone, nevertheless during bulk copolymerization of these substances - using no catalyst, and initiating the reaction simply by warming the mixture from -80°C to room temperature - EPR signals in the vicinity of $g = 2.00$ (the free radical region) having readily measurable intensities could be observed. Sealed glass EPR sample tubes, 5 mm o.d., filled with physically separated, equivolume portions of (solid) BCH and (liquid) SO_2 under nitrogen atmosphere at low temperature, were used in this work. After warming quickly to room temperature, these samples could be placed in the EPR spectrometer sample cavity and the associated EPR signal lineshapes and intensities then followed during the subsequent growth of copolymer. Typical variation of EPR signal intensity with time for such a bulk copolymerization is shown in Figure 2. As indicated in this figure, the number of free radicals increases to a broad maximum in an hour or so, persisting in measurable concentrations for more than a week. (Recent measurements have indicated appreciable radical concentrations persisting for over five months.)

While it is clear that substantial numbers of free radicals accompany this bulk copolymerization, it has not yet been determined exactly where these radicals reside. Experimental limitations have thus far hampered efforts to localize the origin(s) of the EPR signals, except that regions physically near the growing copolymer - BCH interface are involved; whether these are at the visible copolymer - BCH interface itself, or slightly ahead of this interface in the BCH phase, or slightly behind in the copolymer phase, has not been determined. Regardless of the points of origin of these EPR signals, it can be very conservatively estimated that free radical concentrations in excess of 10^{-5} molar are involved; this is to be compared with radical concentrations of about 10^{-8} molar in most normal, steady-state, free radical reactions[4].

The observed EPR (absorption derivative) lineshape at 9.6 KMC spectrometer frequency is shown in Figure 3. Only this one complex lineshape, regardless of the time elapsed after initiation of copolymerization, the portion of sample scanned, or minor variations in polymerization procedure, has ever been observed. Present data are insufficient to determine whether this quite asymmetric lineshape is due to (a) the superposition of EPR signals from two distinct radical species (presumably,

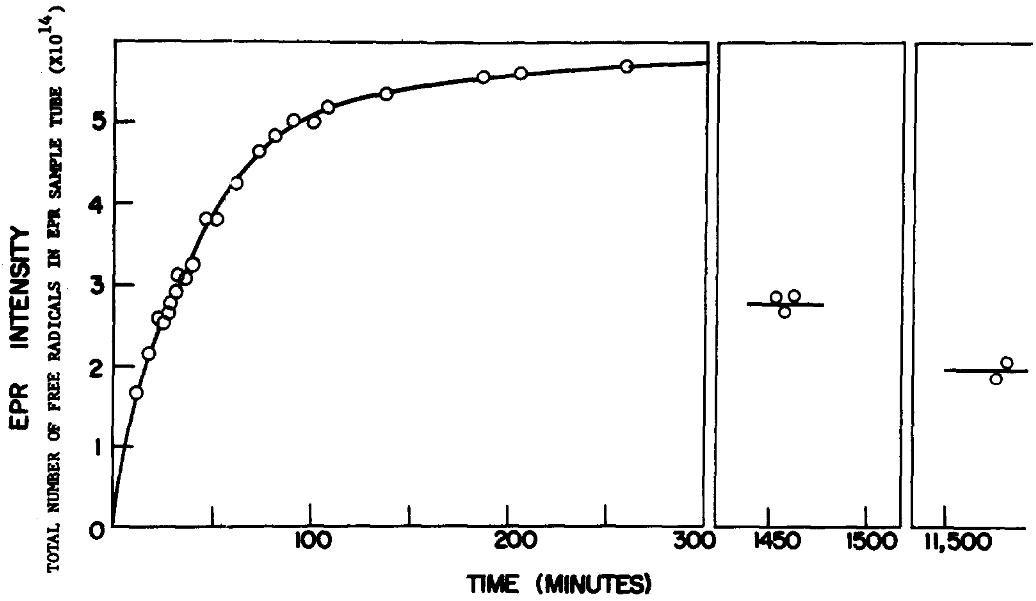


FIGURE 2

EPR Signal Intensity vs. Time from the Heterogeneously Bulk-Copolymerizing Bicycloheptene-Sulfur Dioxide System at Room Temperature.

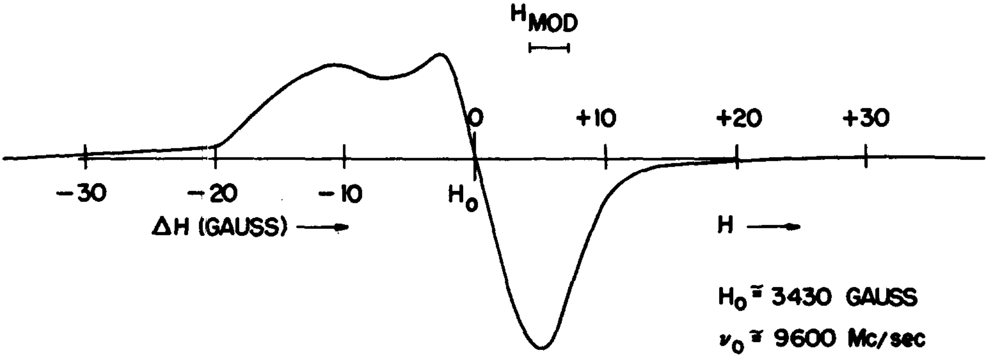
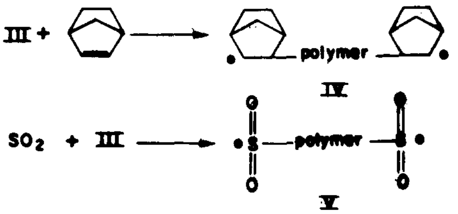


FIGURE 3

EPR Absorption Lineshape Derivative from the Heterogeneously Bulk-Copolymerizing Bicycloheptene-Sulfur Dioxide System at Room Temperature. (Smoothed composite of five experimental curves.)

$-SO_2\cdot$ and $-BCH\cdot$) having slightly different g-values or (b) a single species of radical having restricted mobility and g-anisotropy. If (a) is the case, one radical species occurs at any instant about 3.3 times as abundantly as the other; if (b) is so, a single radical species must preponderate to the extent of 90% or more. Further experiments, at a higher EPR spectrometer frequency and/or at various other sample temperatures, are needed to resolve this ambiquity. These are currently in progress.

In either event, it is clear that the EPR spectra, while revealing large numbers of free radicals during bulk copolymerization, do not support solely the existence of structure III, which would predict $-BCH\cdot$ and $-SO_2\cdot$ radicals in equal abundance. However, if it should happen occasionally, or perhaps frequently, that the following reactions should occur:



then structure IV (or V), which type being dependent both upon its formation energy as well as the monomer concentrations in its vicinity, might rapidly predominate. If structure II is in fact a very short lived intermediate, as is anticipated, the observed EPR spectra could then be expected to arise largely from a single radical structure, either $-SO_2\cdot$ or $-BCH\cdot$, in qualitative agreement with either of the previously stated interpretations of the asymmetric EPR lineshape.

The observed facts that bulk copolymer growth occurs at the copolymer - BCH interface (rather than at the copolymer-SO_2 interface), and is rate-controlled by the diffusion of SO_2 through the copolymer layer, suggest that copolymer is formed in an environment rich in BCH, and hence that structure IV, rather than III or V, might be in greatest abundance. Present evidence is not sufficient, however, to rule out the possibility that (perhaps due to a lower energy of formation) structure V might be the preferred form.

EPR measurements during solution copolymerizations revealed undetectably small radical concentrations (less than about 10^{-7} molar). In light of the fact that copolymerization in solution is essentially complete after a minute or so, this absence of detectable radical concentrations is not surprising, since several minutes were required to make the initial EPR measurement in each of these investigations.

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