Spontaneous polymerization of styrene in the presence of acid: further confirmation of the Mayo mechanism

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Flory and Mayo have proposed alternative mechanisms to explain the spontaneous polymerization of styrene. Both involve the formation of reactive styrene dimers capable of generating initiating radicals. However, the dimer intermediate proposed in the Mayo mechanism has defied all attempts at isolation. Since the Flory dimer would be expected to be stable to acid while the Mayo dimer would not, spontaneous styrene polymerization was studied in an acid environment to determine the effects on oligomer structure, polymerization rate, and polymer molecular weight. The results clearly show that the initiating Mayo dimer is deactivated by acid, forming high levels of inactive dimer. The decreased initiation results in a lower concentration of growing polymer chains, subsequently lowering the rate of termination (by chain coupling). The end result is a large shift of the spontaneous rate–molecular weight relation for polystyrene.

(Keywords: styrene polymerization; initiation mechanism)

INTRODUCTION

The self-initiated (spontaneous) polymerization of styrene has challenged researchers and has received considerable attention over the past 50 years. Two mechanisms explaining spontaneous styrene polymerization have been proposed and supported by considerable circumstantial evidence. The oldest mechanism, first postulated by Flory[1] (*Scheme 1*), involves a bond-forming reaction between two molecules of styrene (S) to form a 1,4-diradical (·D·). The diradical abstracts a hydrogen atom, forming a monoradical initiator (HD·), which reacts with more styrene to yield polystyrene (PS).

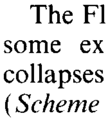
Pryor[2,3] showed that the spontaneous polymerization kinetics of styrene were bimolecular, and again postulated the ·D· intermediate. Further evidence favouring this mechanism includes (1) the identification of *cis*- and *trans*-1,2-diphenylcyclobutanes as the major dimers[4], and (2) the large differences between spontaneous and chemically initiated (azobisisobutyronitrile) styrene polymerizations in the presence of the free radical scavenger 1,1′-diphenyl-2-picrylhydrazyl (DPPH). The rate of consumption of DPPH is 25 times that expected from rate-of-polymerization measurements. This difference was explained by the spontaneous formation of ·D· intermediates, many of which become self-terminated before initiating polymer radicals[5].

The second mechanism (*Scheme 2*) was proposed by Mayo[6]. The mechanism involves the Diels–Alder reaction of two styrene molecules to form a reactive dimer (DH) (*alpha*-regioselective), followed by a molecular assisted homolysis (MAH) between DH and another styrene molecule. The Mayo mechanism has been generally preferred, even though critical reviews[2,3] have pointed out that the mechanism is only partly consistent with the available data. Also, the intermediate DH has never been isolated. Evidence supporting the mechanism includes kinetic investigations[7,8], isotope effects[2], and isolation/structure determination of oligomers[2,9]. Even though DH has never been isolated, the aromatized derivative DA has been detected in polystyrene[9]. Also, D· has been indicated as an end-group in polystyrene, using ^{1}H n.m.r. and u.v. spectroscopy[10].

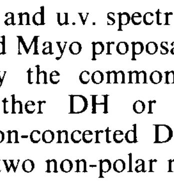
The Flory and Mayo proposals could be combined to some extent by the common diradical ·D·, which collapses to either DH or 1,2-diphenylcyclobutane (*Scheme 3*). Non-concerted Diels–Alder reactions are permissible for two non-polar reactants[11].

Trimer T could possibly be formed by two routes: (1) MAH followed by radical combination, or (2) a concerted Alder ene-reaction between S and DH. Frontier molecular orbital calculations between the HOMO of DH (ene) and the LUMO of styrene (enophile) predict that an Alder ene-reaction would yield the β-phenethyl derivative (*Scheme 4*) as the major product[12]. However, only the α-phenethyl derivative has been reported, indicating that radical combination rather than the Alder ene-reaction is the predominant path.

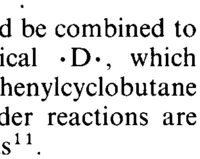
Several models of DH have been synthesized and tested as MAH initiators. They include 5-methylene-1,3-cyclohexadiene (MCHD)[13], the adduct of 4-phenyl-1,2,4-triazoline-3,5-dione with 2-vinylthiophene (PTVT)[14], and 1,2,3,10-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (THPA)[15]:



MCHD



PTVT



THPA

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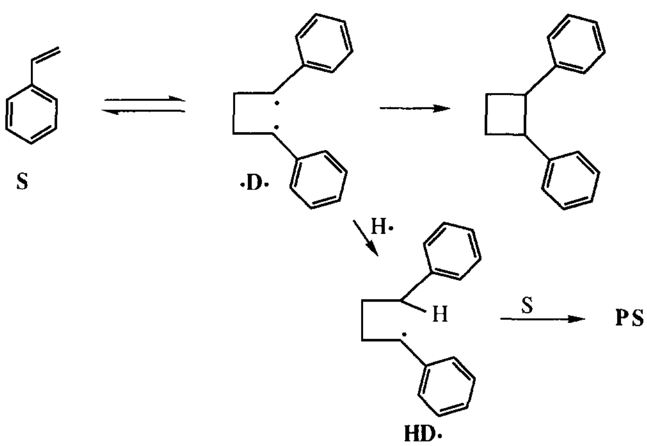
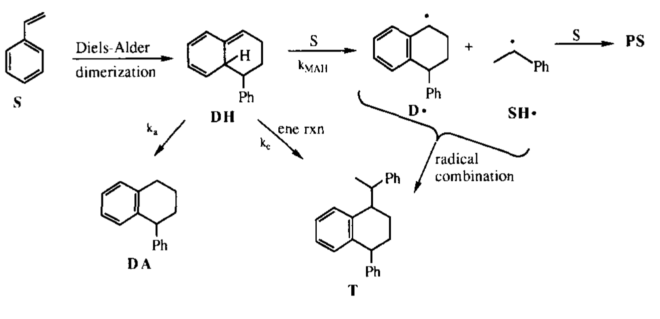
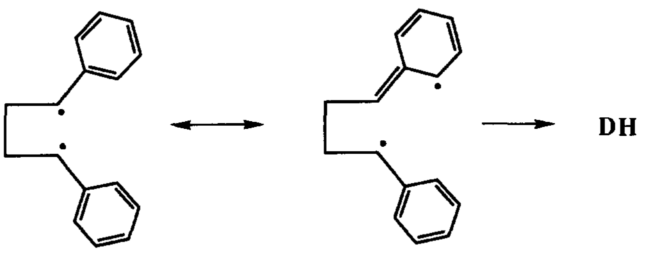


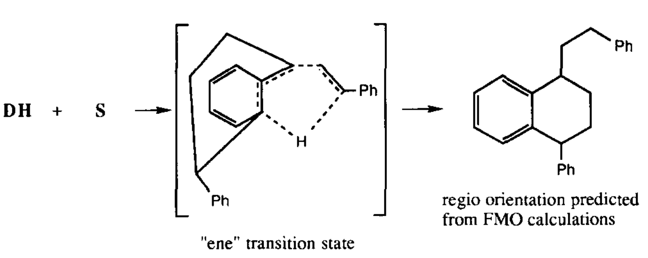
Scheme 1 Flory mechanism for spontaneous initiation of styrene polymerization



Scheme 2 Mayo mechanism for spontaneous initiation of styrene polymerization



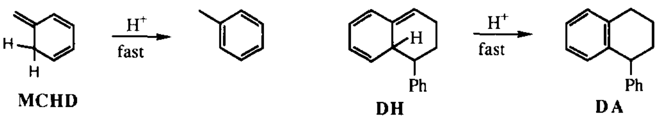
Scheme 3 Formation of the Mayo dimer via the Flory diradical



Scheme 4 Predicted regiochemistry (frontal molecular orbital (FMO) theory) of trimer formed via the ene-mechanism

Both PTVT and THPA were found to be MAH initiators for styrene: however, MCHD gave almost entirely the ene-adduct with styrene. Also, MCHD was found to aromatize rapidly to toluene in the presence of certain acids[16].

The relative amounts of DA reported in the various studies differ greatly. Levels ranging from 2%[17] to 70%[18] of the total dimeric fraction have been reported. The rapid isomerization of DH to DA by different levels of adventitious acid has been suggested to explain these large differences[19]:



The present authors chose to investigate the spontaneous polymerization of styrene in the presence of various acid catalysts to see if the postulated reactive intermediate DH could be intentionally aromatized to form inactive DA at a faster rate than the MAH (i.e., $k_a > k_{MAH}$). A finding that the rate of polymerization of styrene is significantly retarded by acids, accompanied by increases in the formation of DA, would provide further confirmation of the intermediacy of DH, since acids would have little effect on the cyclobutane dimer intermediate in the Flory mechanism.

EXPERIMENTAL

Materials

Styrene (Dow Chemical Company) contained 3 ppm of *t*-butylcatechol. Spectral-grade methanol and tetrahydrofuran (THF) (Fischer Scientific Company), and acetic (99%), benzoic (≥99%), pyruvic (98%), phenylphosphonic (98%), and (+/−)10-camphorsulphonic (99%) acids (Aldrich Chemical Company) were used without further purification. The peroxide initiator *t*-butyl perbenzoate was obtained from Akzo Chemicals.

Ampoule polymerization

The acid being investigated was placed in a glass ampoule (7 mm o.d. x 5 mm i.d.) with the desired amount of styrene. The ampoule was frozen in dry ice, sealed under vacuum (<0.5 mmHg), and placed in a hot oil bath and allowed to cool to room temperature before being frozen again and opened.

Analysis

Conversion was determined by vacuum-drying the syrup at <0.5 mmHg and 225°C for 15 min. Polymer was isolated for g.p.c. analysis by precipitation in methanol, followed by 16 h drying under ambient conditions. The weight-average molecular weight (M_w) of the polymer was measured by g.p.c. on a Hewlett-Packard HP1090A liquid chromatography system, fitted with two 30 cm PL-gel 5μ columns connected in series. Samples were prepared by dissolving the purified polystyrene to 0.25 wt% in THF.

Oligomer analyses were performed using liquid chromatography under conditions previously described[20], or by g.c.–m.s. For the latter, the polymer was dissolved in methylene chloride and precipitated by the addition of methanol. The column used was a 7 m × 0.18 mm DB-1 (methyl silicone) with a 0.4 μm film thickness. The oven was programmed with an initial temperature of 70°C for 2 min, then ramped at 15 K min^{-1} to 355°C for 15 min, while the injector was programmed with an initial temperature of 70°C for 0.01 min and a temperature ramp of 500 K min^{-1} to a final temperature of 350°C for 30 min. The transfer line temperature was held constant at 355°C. The m.s. detector was set to scan

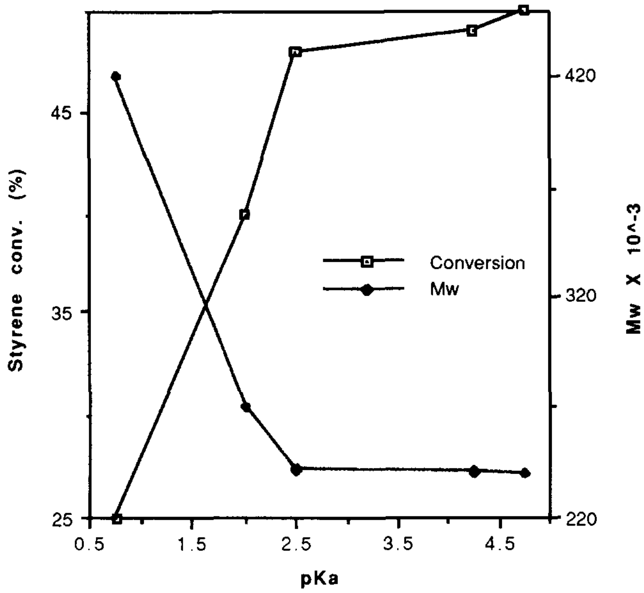


Figure 1 Effect of acid strength on styrene conversion and M_w of PS

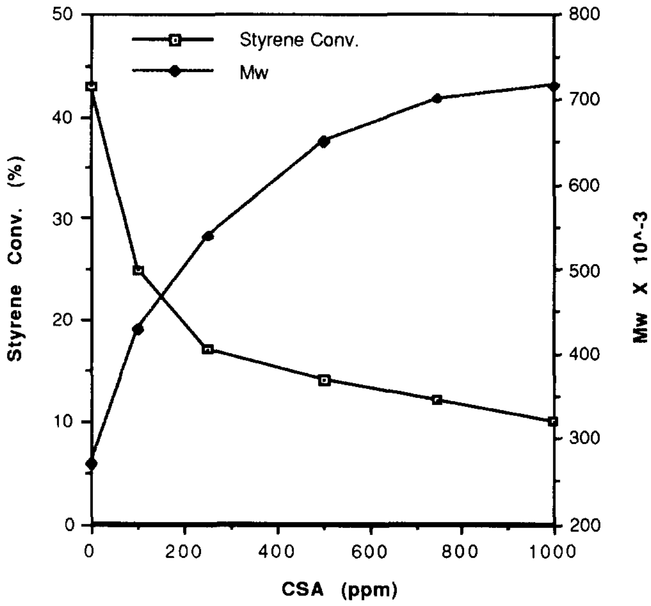


Figure 2 Effect of CSA concentration on styrene conversion and M_w of PS

from 35 to 650 m/z with two scans per second and a solvent delay time of 3 min. All spectra were background-subtracted. The structure of the oligomers was identified by comparison of spectra with the Wiley 130K Mass Spectral Library. The main oligomer peak was identified as 1-phenyl-1,2,3,4-tetrahydronaphthalene with a quality of 97%.

RESULTS AND DISCUSSION

It is well known that styrene rapidly polymerizes at ambient temperatures via a cationic mechanism in the presence of strong acids (e.g. sulphuric acid). These acid-initiated polymerizations are usually extremely rapid, producing low-molecular-weight polymers. With this in mind, acids were chosen for evaluation that would dissolve in styrene without evidence of polymer formation. Acids such as methanesulphonic and trifluoroacetic were eliminated as candidates, because they gave evidence of polymer formation upon addition to styrene at ambient temperature. Styrene samples, with and without added acid, were then sealed in glass ampoules and heated to produce polystyrene (PS). The effects of each acid on the polymer molecular weight, polymerization rate, and dimer/trimer level were determined.

Five acids covering a broad range of pK_a were selected for further evaluation. These acids are soluble in styrene and do not catalyse cationic polymerization at ambient temperature. The acids were dissolved in styrene at a concentration of 0.1 mol%. The styrene mixtures were heated at 150°C for 1 h. *Figure 1* shows the effects of the acids on the amount of styrene converted to PS, and the molecular weight of the polymer produced. These results clearly show that the presence of strong ($pK_a < 2$) acids retard the rate of polymerization.

Of the acids evaluated, camphorsulphonic acid (CSA) had the greatest effect on the polymerization kinetics, and was the strongest acid. Even though there was no sign of cationic polymerization when a solution of styrene containing CSA was allowed to stand at ambient temperature, the question still remained as to whether the polymerization mechanism was truly only free-radical. To answer this question, it was suggested[21] that a non-basic nucleophile be added, to see if there was any change in the polymerization rate and molecular weight behaviour observed in *Figure 1*. If the mechanism involved the formation of a carbocation chain-end, this would quickly add to the nucleophile and terminate. Therefore triphenylphosphine (0.1 w/w) was added to a styrene polymerization containing 500 ppm CSA. There was no change in the polymerization rate or molecular weight.

The effect of CSA concentration on styrene conversion and molecular weight at 140°C is shown in *Figure 2*. The effect of addition of CSA in increasing M_w is observed over a broad temperature range (*Figure 3*). M_w of the PS increases with acid concentration, while at the same time the monomer conversion decreases. The same trend can also be created in the thermal polymerization of styrene by varying the temperature (*Figure 4*).

The combination of *Figures 3* and *4* shows that the

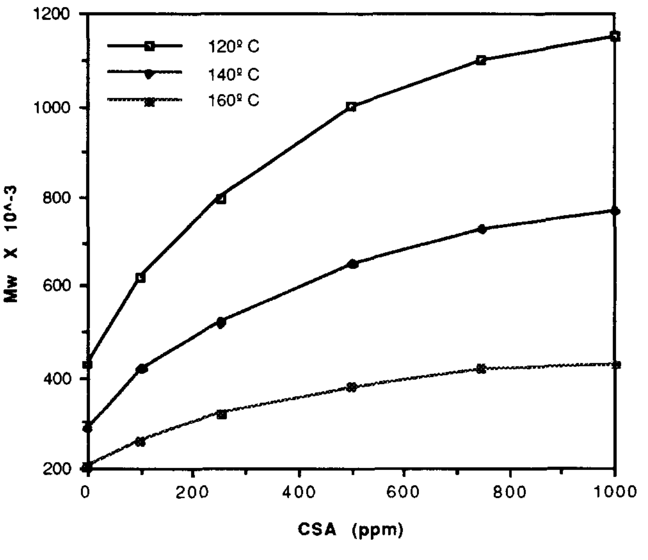


Figure 3 Effect of CSA concentration on M_w of PS at different temperatures

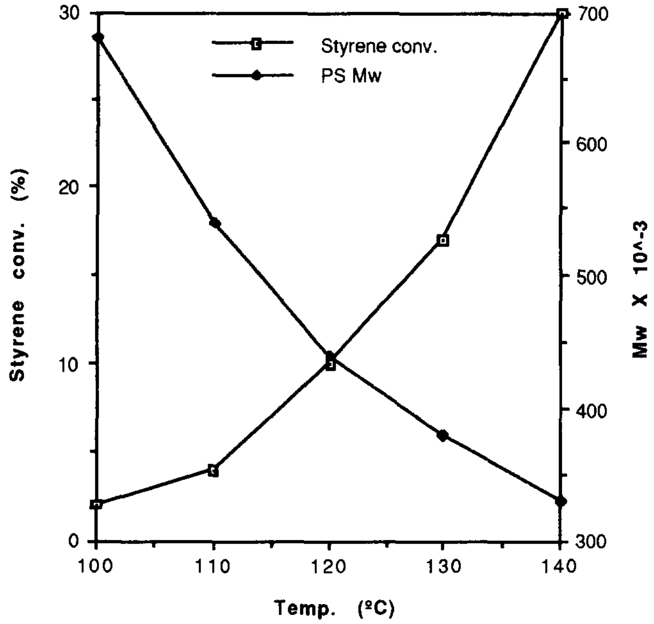


Figure 4 Effect of polymerization temperature on M_w of PS and styrene conversion after 1 h of isothermal heating

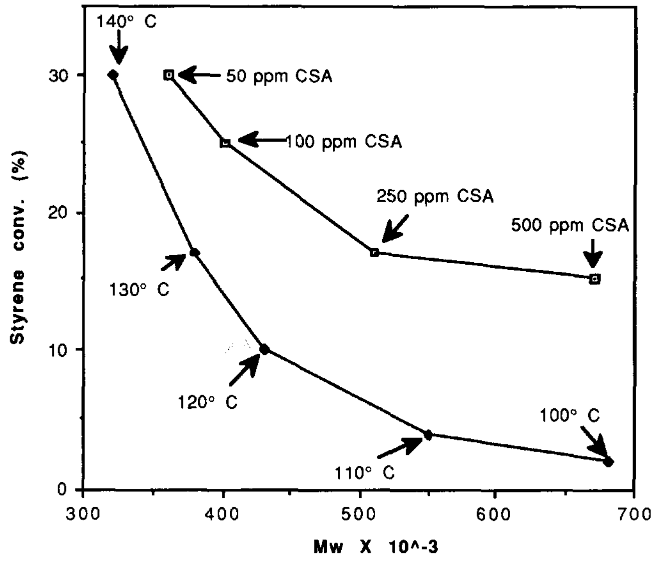


Figure 5 Comparison of polymerization rate–M_w relation for PS obtained at various temperatures without acid (lower curve) with that for PS obtained at 140°C in presence of various CSA concentrations (upper curve)

PS rate–M_w relation is significantly improved by the addition of CSA; for example, PS of M_w 680 000 can be produced five times as fast in the presence of 500 ppm CSA (*Figure 5*). This represents a method of significantly departing from the normal rate–M_w relation for spontaneous styrene polymerization.

The production of dimer DA and trimer T as a function of acid level was measured in ampoule polymerizations after 5 h at 140°C. The concentration of DA in the polymer syrup rose when acid was introduced and continued to rise as the acid level was increased, while the T level decreased (*Figure 6*).

Kinetic studies were performed in ampoules at a concentration of 580 ppm CSA and a temperature of 140°C. As the polymerization time increased, monomer conversion increased, while M_w remained relatively constant (*Figure 7*). DA formation increased with polymerization time and T formation held its inverse relation to DA formation, its concentration decreasing slightly in the polymer syrup over the course of the polymerization (*Figure 8*). The CSA concentration during the run remained constant, demonstrating that it acts catalytically.

Another surprising observation is the high levels of DA produced during the extended polymerization (*Figure 8*). This indicates that not only is the CSA catalysing the aromatization of DH to DA, but it may also be catalysing the Diels–Alder reaction leading to DH formation. Protonic acids have been shown to catalyse Diels–Alder reactions[22–24].

A search of the literature revealed that this is not the first time that acid has been added to a free-radical vinyl polymerization. In a recent study[25], acid was added

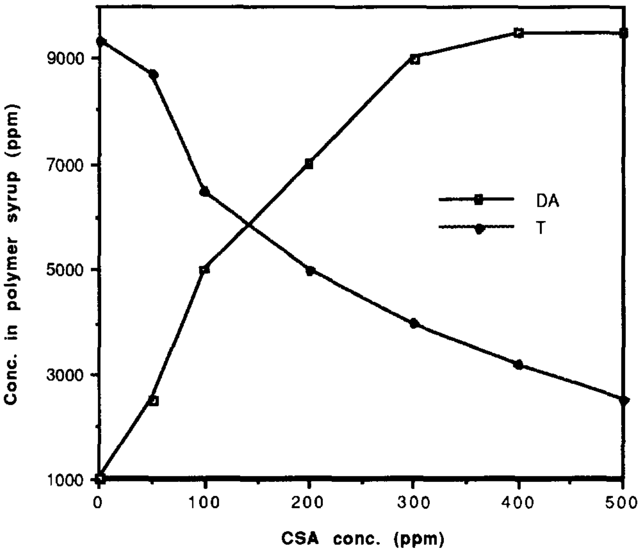


Figure 6 Effect of CSA concentration on DA and T levels after 5 h at 140°C

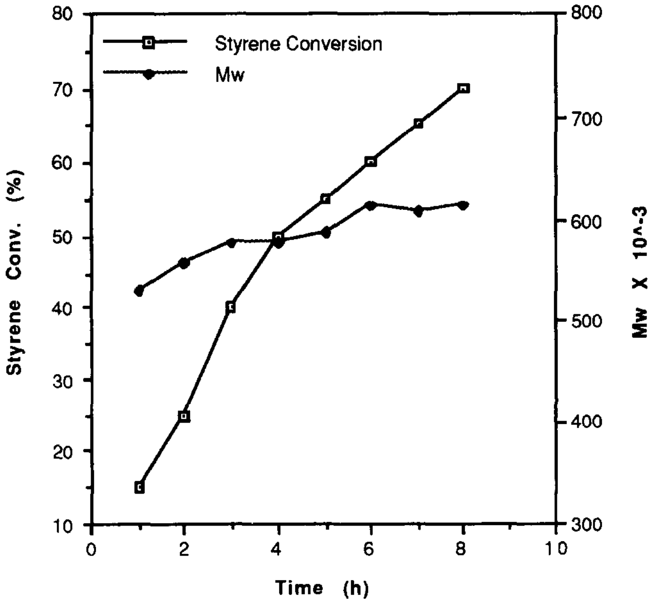


Figure 7 Changes in styrene conversion and M_w of PS during isothermal polymerization at 140°C in presence of 580 ppm CSA

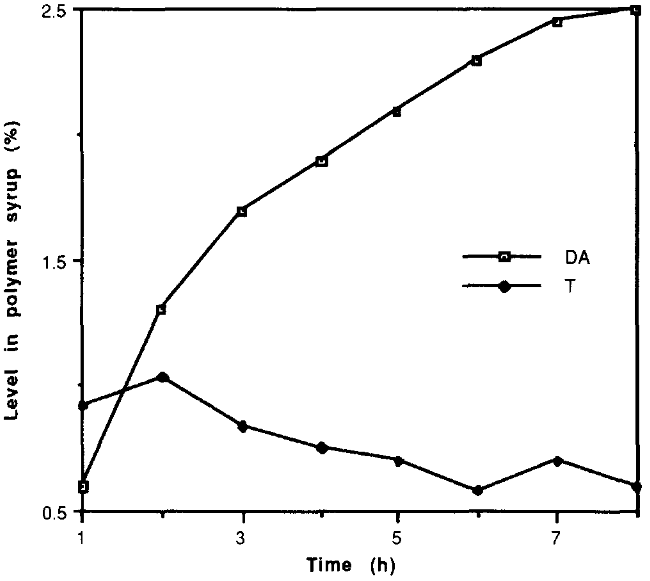


Figure 8 Formation of DA and T as a function of polymerization time at 140°C in presence of CSA

to the peroxide-initiated polymerization of methyl methacrylate to induce the decomposition of the peroxide initiator. No mention was made of molecular weight increases or polymerization rate retardation; on the contrary, addition of the acid resulted in increases in the rate of polymerization. The present authors in fact found virtually no difference in conversion or PS M_w when polymerizing styrene containing 1000 ppm of *t*-butyl-perbenzoate at 130°C with and without 500 ppm CSA. In the presence of a peroxide, initiation is no longer dependent upon the formation of DH, so its acid-catalysed aromatization to DA has little effect on polymerization kinetics.

CONCLUSIONS

The results reported are consistent with the Mayo mechanism. The reactive Diels–Alder dimer DH quickly aromatizes to inactive DA in the presence of acid catalyst. This results in a decrease in the rate of initiation and a decrease in the formation of trimer T, because DH is the precursor of both. Increasing the polymerization temperature to compensate for the decreased rate of initiation increases the propagation rate. Since the concentration of growing polymer chains is low owing to decreased initiation, the rate of termination (by chain coupling) is decreased. The result is that a PS of M_w much higher than expected is produced. Addition of a peroxide initiator counteracts the effects of the acid by changing the mechanism of initiation and maintains a high level of growing polymer chains, recovering the normal rate of termination by coupling.

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