Examination of the Preparation of a Block Copolymer from Macroradicals Produced in Viscous Media

Pierre E. J. Louis, Robert G. Gilbert,* and Donald H. Napper

School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

Philippe Teyssié and Roger Fayt

Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Université de Liège, Sart-Tilman (B 6), 4000 Liège, Belgium

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ABSTRACT: Extensive experiments on copolymer syntheses as a type of dispersion polymerization in viscous poor solvents (e.g., silicone oil) have been reported (Seymour, R. B.; Kincaid, P. D.; Owen, D. R. *Adv. Chem. Ser.* 1973, *129*, 230) which, based on a trapped-macroradical model, were taken to suggest that such conditions promoted the formation of block copolymers. Here we report the results of a series of tests devised to elucidate the mechanisms in these systems. One such test used initiation by γ radiolysis of water, which allows virtually instantaneous cessation of the production of primary radicals after removal from the γ source. This resulted in a very rapid drop in the polymerization rate. This observation constitutes what seems to be irrefutable evidence against the trapped macroradical model, which would predict that the polymerization should continue at a moderate rate after removal from the source. Furthermore, it is shown that in these viscous-solvent dispersion polymerizations, there is a significant rate of production of free radicals under conditions where the original interpretation implied that this would not be the case. Moreover, it is shown that the formation of graft copolymers can result from the transfer reaction of primary free radical with the preformed homopolystyrene backbone. The original erroneous interpretation (in terms of formation of block copolymers from trapped macroradicals) can thus have arisen because the distinction between block and graft copolymer was beyond the resolving power of the analytical technique used to characterize the products. The results of the present experiments and those of Seymour can be readily explained in terms of rapid termination between two long macroradicals encountering each other through reaction/diffusion and/or between an entangled macroradical and a mobile oligomeric free radical formed by transfer.

Introduction

Block copolymers are of considerable technical importance: for example, as compatabilizers for polymer blends or as organized heterophase materials. There is thus a need to be able to prepare block copolymers from as wide a variety of monomers as possible. Most such block copolymers are prepared by ionic (usually anionic) methods. Preparation by free-radical polymerization potentially represents a useful alternative synthetic approach for such an objective, as it is applicable to many more monomeric species and is comparatively easier and less expensive to handle than ionic methods.

An ideal means for free-radical production of a pure block copolymer would involve growing homopolymer of monomer A under conditions such that, at a certain time, no further A was available for polymerization, and the rate of termination could be made zero; living A macroradicals would then remain. Monomer B would then be introduced under conditions such that no new chains could be formed by transfer; under these idealized conditions, the only product would be an A–B block copolymer.

Free-radical methods that have been claimed to result in block copolymers include the flow method described by Hicks and Melville,[1-3] the use of prepolymers with active end groups reported by Bamford and Jenkins,[4,5] and the use of a polymeric photoinitiator.[6,7] One particularly simple path is the use of long-lived polymer radicals: this is most attractive for block copolymer synthesis as it does not require reactions any more complicated than those involved in classical free-radical polymerization processes; furthermore, it can be run as a "one-pot reaction".

A number of workers have reported a series of carefully designed experiments which were purported to be of the "ideal" type as described above: when growing macroradicals are produced in an environment in which normal termination rates are diminished and the chain lifetimes therefore extended, sequential polymerization with a second monomer should in principle take place with the formation of block copolymers. The first exploitation of such a strategy was reported by Bolland and Melville for the formation of a block copolymer by addition of chloroprene to methyl methacrylate macroradicals trapped in the polymer film.[8,9] Bamford and Jenkins demonstrated that solid poly(acrylonitrile), prepared by photopolymerization at 25 °C, polymerizes further with acrylonitrile or styrene if heated at 60 °C.[10] However, the products do not include much of the second monomer (ca. 5%). Extension of this work by Hiemeleers and Smets yielded no more than 16% of the second monomer included in the block copolymer.[11]

In contrast to these fairly low values, Seymour and co-workers have reported quite a high level of second monomer incorporation: up to a 100% increase in the molecular weight with up to an 88% block copolymer yield in the case of poly(styrene-*b*-methyl methacrylate).[12] These block copolymers were reported to be produced when a vinyl monomer is added to a suspension of trapped macroradicals in a poor solvent, provided that the difference in the solubility parameter values of the monomer and the macroradical is not greater than 3.1 Hildebrand units.[13] With the aim of ensuring that, at the moment when the second monomer is injected into the polymerization vessel, there would be no more primary free-radical production possible via the first initiator, Seymour and co-workers left the system at 50 °C for a long period (typically 96 h) before injecting the second monomer and assumed that all the initiator molecules were decomposed by the end of this second stage.[14-16] They interpreted their experiments

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* Author to whom all correspondence is addressed.

to be examples of the ideal type described above: living macroradicals of homopolymer remain at the end of the second stage, unable to undergo mutual termination because of the high viscosity of the medium; block copolymers are accordingly supposed to be formed on addition of the second monomer, with little formation of homopolymer. If the initiation of the second block is really due to some living trapped radicals and not to some residue from the initiator of the first sequence, one should be able to produce the same type of block copolymers by using an initiator system for the first block which could be physically removed from the medium prior to the addition of the second batch of monomer. In what was claimed to be an example of this strategy, Horie and Mikulasova used partially oxidized polypropylene as the primary initiator in an emulsion system.[17] They claimed that this initiator species can be physically removed from the reaction vessel by filtration before any further studies. Production of more than 80% of P(S-*b*-MMA) was reported by using this method.[18,19] Even for such an emulsion system, the question still arises as to the efficiency of the filtration process and the validity of the tests performed.

The viscous-solvent method of production clearly has the potential for important technical applications, as well as being worthy of investigation on purely scientific grounds. The overall objective of this present paper is to investigate further the mechanism originally suggested to explain the experimental observations. Since the original work by Seymour and co-workers, new experimental and theoretical techniques have become available to elucidate mechanisms at high conversion in heterogeneous polymerizations.[20] We here report the results of the application of some of these techniques to this potentially important system.

The question arises as to whether or not the initiation of the second block is really due to trapped macroradicals. We present the results of four separate tests of the trapped-macroradical hypothesis, of a type such that the results of the tests have the capability of actually *refuting* this hypothesis[21] if positive or supporting it if negative. The tests we use (given in the detail below) are typified by the following example (actually denoted "Experiment 3" in a later section of this paper). The first stage of the polymerization employs a dispersion of styrene dissolved in silicone oil (a suitable viscous solvent) in water. γ radiolysis of the water is used to produce $^{\bullet}$OH primary free radicals, and polymerization is allowed to proceed for a suitable time. Primary free-radical production is then switched off essentially instantaneously by the removal of the reactor from the ^{60}Co source,[22] while the polymerization is followed by precision dilatometry. If the trapped-macroradical hypothesis were correct, then polymerization should continue at a moderate rate upon removal from the source; if, on the other hand, the rate of polymerization decreased extremely rapidly upon removal from the source, then the hypothesis would have been refuted.

Experimental Section

Poly(ethylene glycol) (PEG) of MW 400, poly(propylene glycol) of MW 4000, and silicone oil of viscosity 300 cP (Aldrich Chemical Co., Inc.) were deoxygenated by bubbling high-purity-grade nitrogen through for at least 30 min and/or by degassing under vacuum.

Styrene and methyl methacrylate (Ajax Chemicals; L.R. grade) were distilled under reduced pressure and used within 0.5 h.

2,2′-Azobis(isobutyronitrile) (AIBN; Merck) was analytical grade and recrystallized from methanol. *tert*-Butyl peroxypivalate (tBPP; Interox), 75% in mineral spirits, was used as received.

Triply distilled water was degassed before use; solvents used for selective extractions were analytical grade from Merck.

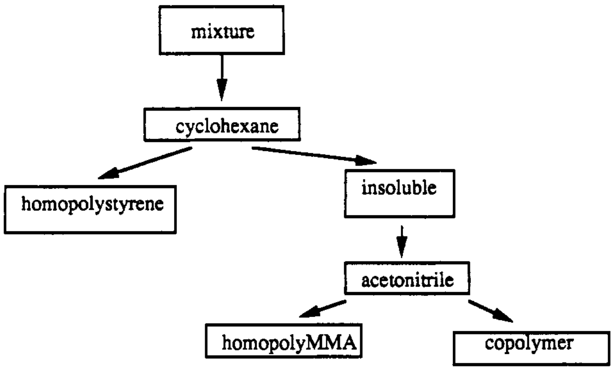

Figure 1. Selective extraction scheme for a mixture of S/MMA polymers.

Evolution of the polymerization was tracked by automated precision dilatometry. The 12.4 krad h^{-1} ^{60}Co source was designed in such a way that the dilatometer could be removed from the source within less than 5 s.

Results and Discussion

Experiment 1. The purpose of our first experiment is to duplicate the type of experiment performed by Seymour and co-workers,[12] including testing the effects of using an alternative viscous solvent (poly(ethylene glycol) as well as silicone oil), and critical examination of the results using analytical techniques developed after Seymour's original work was carried out.

At time $t = 0$, 50 g of PEG, of molecular weight 400, 5 mL of styrene, and 0.25 g of AIBN were mixed and allowed to react at 65 °C in two identical reactors for 8 h. Then, at time $t = 8$ h, one of the reactors was opened and the product of the reaction poured into an excess of methanol while 5 mL of MMA was added to the second reactor. After 24 h, the second reactor was opened and the contents poured into 2 dm^3 of methanol. The polymers produced were recovered by filtration and washed with methanol, in which the poly(ethylene glycol) is soluble.

Gravimetric determination gave a conversion of 95% of the styrene after 8 h and 100% conversion for both monomers after 32 h. In order to separate and quantify the components produced in the system to which MMA had been added, the raw material was submitted to successive extractions by selective solvents, as described in the literature,[23] and shown in the scheme of Figure 1. The results of these extractions are summarized in Table I. Three fractions were collected: homopolystyrene, homopoly(methyl methacrylate), and some supposedly block copolymer. The IR spectra of the homopolymer fractions indicated that they were nearly pure homopolymers, since intensities of peaks belonging to other monomeric species were less than 5% of those of the homopolymer.

In addition to these selective extractions, the crude product was submitted to orthogonal HPLC/SEC chromatography coupled with ^{1}H NMR spectrometry analysis. This analytical method, described elsewhere,[24] gives the chromatogram shown in Figure 2. This shows three peaks assigned to homopolystyrene (HPS), to some statistical copolymer, P(S-*co*-MMA), and to another copolymeric species, P(S-*b*-(S-*co*-MMA)). A similar set of experiments, but with a temperature of 60 °C and with silicone oil replacing the poly(ethylene glycol), were also carried out. The percentages of these fractions are also shown in Table I.

On the basis of the selective extraction results, one would be tempted to think that viscous-solvent dispersion polymerization in silicone oil can be transposed to PEG 400, another viscous poor solvent for polystyrene. However,

Table I
Composition of the Polymer Mixture Deduced from Selective Extractions and from HPLC/^{1}H NMR Analysis[24,a]

viscous solvent	silicone oil	PEG
temp, °C	60	65
initiator half-life, h	18	8
t_1, h	96	8
convn at t_1, %	100	85
t_2, h	96	24
HPS (SE), %	43	25
HPMMA (SE), %	39	9
copolymer (SE), %	18	66
HPS (NMR/HPLC), %		27
P(S-*co*-MMA) (NMR/HPLC), %		60
P(S-*b*-(S-*co*-MMA)) (NMR/HPLC), %		13

[a] t_1 = time at which second monomer added. t_2 = time after t_1 at which reaction products were analyzed. Gravimetric analysis showed 100% conversion for both reactions at t_2. HPS (SE), HPMMA (SE), and copolymer (SE) are homopolystyrene, homopolyMMA, and copolymer contents analyzed by selective extractions. HPS (NMR/HPLC), P(S-*co*-MMA) (NMR/HPLC), and P(S-*b*-(S-*co*-MMA)) (NMR/HPLC) are percentages of homopolystyrene, statistical polymer, and partial block copolymer, analyzed by the combined NMR/HPLC technique.

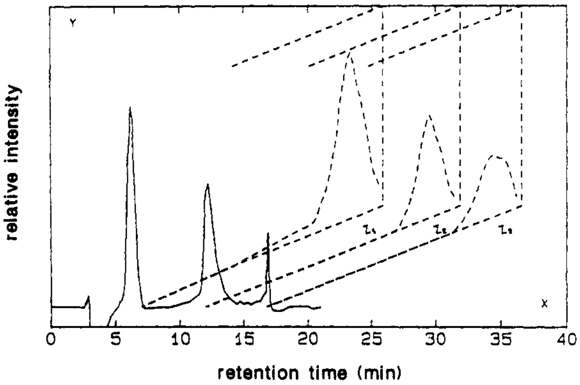

Figure 2. HPLC/SEC orthogonal chromatography of the raw material produced in experiment 1 (PEG as the viscous solvent). The HPLC chromatograms are in the *xy* plane for fractions at different retention times (Z_1, Z_2, Z_3) from size-exclusion chromatography.

product analysis of our results using HPLC and ^{1}H NMR, a much better technique for copolymer analysis, is in disagreement with the results obtained from the simpler selective extraction procedure. This indicates that extraction procedures are not selective enough for quantitative copolymer analysis for systems such as these. This implies that (despite its occasional current usage for this purpose) selective extraction is not suitable for a proper segregation between statistical and block copolymers and is likely to lead to an overestimate of the amount of block copolymer when some statistical copolymer is also produced in the reaction.

Given the uncertainty of the results from the selective extraction measurements, what is the likely product of these experiments, if not a block styrene/MMA copolymer? Now, in the experiments using PEG as the viscous solvent, the addition of the second monomer was performed only 8 h after the beginning of the synthesis. Under these conditions, production of the *statistical* copolymer is likely to occur because (a) the first monomer has not yet reached 100% conversion at the time of addition of the second monomer and (b) the initiator is not totally decomposed (the half-life of AIBN at 65 °C is 8 h). Nevertheless, this first experiment clearly points out the weaknesses of the selective extraction analysis method often encountered in the literature.

Experiment 2. The objective of this second experiment is to check the validity of the assumption that, in these viscous-solvent dispersion polymerizations, no significant numbers of new chains are produced on addition of the second monomer: i.e., that all subsequent polymerization arises from the postulated living macroradicals.

In the experiments reported by Seymour and co-workers, the second monomer was generally added to the system 96 h after the beginning of the polymerization of the first monomer. Under these conditions, the assumption of a negligible rate of production of free radicals at the time of the addition of the second monomer apparently seems perfectly reasonable. Indeed, at 65 °C in ethylene glycol, the decomposition rate coefficient of AIBN is 2.5×10^{-5} s^{-1},[25] so that, after 96 h at that temperature, there is less than 0.01% of the initial amount of the initiator left. The purpose of our second experiment was to check the validity of this assumption that there was indeed negligible radical production after 96 h.

At time $t = 0$, 50 g of silicone oil (300 cP), 5 g of toluene (as a substitute for styrene), and 0.25 g of AIBN were mixed at 65 °C and equilibrated with gentle stirring for 96 h. The resulting system was transparent. Then, after 96 h had elapsed, 5 mL of freshly distilled and degassed styrene was added to the medium under a flux of nitrogen. After 10 h, the medium had turned white, suggesting that the styrene was polymerizing. After 7 days, the reactor was opened and the amount of polystyrene was measured gravimetrically. More than 50% of the monomer was converted to polymer (higher precision is rendered difficult because the presence of silicone oil engenders uncertainties in the gravimetric estimation). It is essential to note at this point that the observed rate of polymerization is of the same order as that seen in Seymour's experiments.

The same experiment was performed with tBPP as initiator, again leading to significant polymerization of the styrene. The same procedure was also carried out with ethylbenzene replacing toluene and with MMA replacing styrene; again, the same effect (high conversion of monomer to polymer) was observed.

The initiation of styrene polymerization observed after the 96-h waiting period shows that one cannot neglect the formation of primary free radicals when one adds the second monomer to the system, even with a level of residual initiator of less than 0.01% of the starting level.

Clearly, there is a significant "residual" rate of production of free radicals in these systems at extremely low initiator concentrations. A number of postulates as to their origin might be put forward: (a) residual initiator, (b) thermal polymerization of monomer, and (c) thermal decomposition of peroxides or other impurities present in the reaction mixture. In the context of this last possibility, it is noted[27] that in conventional *emulsion* polymerizations, such "impurities" (which turn out to be inherent in the way the latex is made) give rise to a large and fairly reproducible "thermal" or "background" free-radical production rate.

While the question of the origin of this residual radical production in the present system is of interest, we do not pursue this matter further here. For the present purposes, it is sufficient to note that the results render unnecessary any need to postulate the existence of the trapped-macroradical hypothesis. This postulate implies that most of the second-stage polymerization observed in viscous-solvent dispersion polymerizations is due to propagation of the trapped macroradicals. However, in the experiments reported in this section, there could have been no such living macroradicals present (since there was no polymer present in the first place): nevertheless, the rate of polymer formation in the second stage of the present experiment was comparable to that in Seymour's results.

The foregoing evidence cannot be said to be capable of unambiguously refuting the hypothesis: after all, whatever process is causing the residual polymerization in the present experiment could also be taking place in viscous-solvent dispersion polymerizations (and producing significant amounts of homopolymer of the second monomer), while trapped-macroradical polymerization was also occurring (and producing significant amounts of the true block copolymer).

Experiment 3. The purpose of this third set of experiments is to test the postulate that trapped macroradicals are present in significant quantities after most of the initiator has decomposed in viscous-solvent dispersion polymerizations. The test is the one described in the introduction: viz., initiating the polymerization with γ radiolysis, removing the reactor from the source generating new free radicals, and observing the rate at which polymerization shows. If this decrease were extremely rapid, it would be difficult to reconcile with the fundamental trapped-macroradical hypothesis.

According to the results of the previous experiment, one cannot neglect the production of primary free radical following the introduction of the second monomer. The following experiment was designed in order to bypass the necessity of considering this small residual free-radical production rate. The controlled production of primary free radicals by γ radiolysis of water was used for the initiation step. A total of 1.5 g of styrene was dissolved in 10 g of silicone oil; the solution was then dispersed in 40 g of water by vigorous stirring in a dilatometer. The reactor was lowered into a ^{60}Co source and the subsequent conversion of monomer to polymer measured by dilatometry. Half an hour after the end of the induction period, the dilatometer was removed from the source and the polymerization observed for 30 min before reinsertion into the source. This sequence (in–out) was repeated three times consecutively. The observed conversion and polymerization rate are plotted versus time in Figure 3.

The same experiment was repeated with poly(propylene glycol) (molecular weight 4000) dispersed in water instead of silicone oil. The polymerization was allowed to proceed in the γ source up to 20% conversion before removal of the dilatometer from the source. The subsequent evolution of the system was followed for 72 h as shown in Figure 4.

The radical species formed from the radiolysis of water that can enter the styrene/silicone oil droplets and initiate the polymerization are •OH, •H, and e^-_{aq}.[22,26] The macroradicals so generated will not be terminated by the newly produced free radicals, since entry events only occur about every 20 min,[27] while the postremoval decay is on the order of 5 min[20,27] and since these radical species will cause mutual termination on a time scale of less than 1 ms after removal from the γ source but, being produced mainly in the aqueous phase, will not undergo extensive termination with macroradicals located within the viscous poor solvent (e.g., it is well established that, in styrene emulsion polymerization systems under equivalent conditions, the relaxation rate after removal from the source is on the order of minutes[20]).

Figures 3 and 4 show that, as soon as the reaction vessel was removed from the ^{60}Co source, the rate dropped dramatically to a value close to zero: indeed to a rate per particle that is about that of the thermal contribution observed for a typical emulsion polymerization.[27]

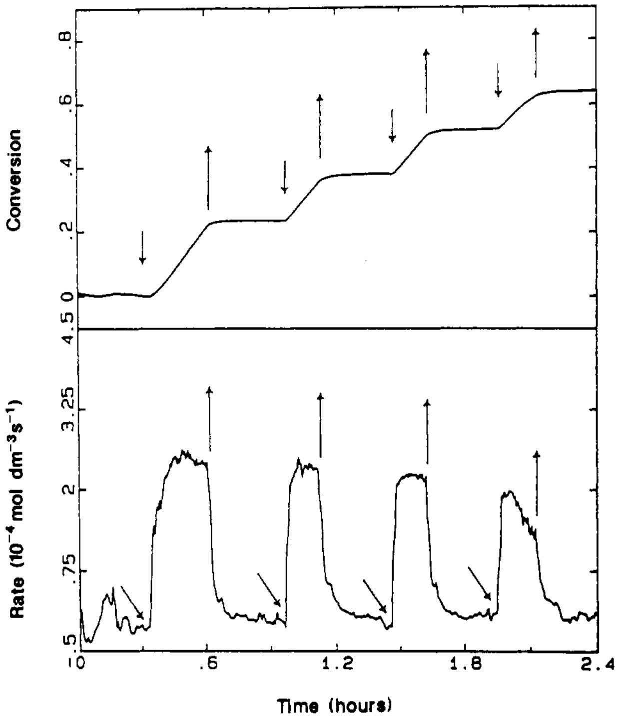

Figure 3. Conversion and polymerization rate for γ-radiolysis-initiated polymerization of styrene in silicone oil (300 cP): T = 50 °C; [styrene] = 1.5 mol dm^{-3}; γ intensity = 12.4 krad h^{-1}. Arrows indicate the times of insertion into and removal from the radiation source.

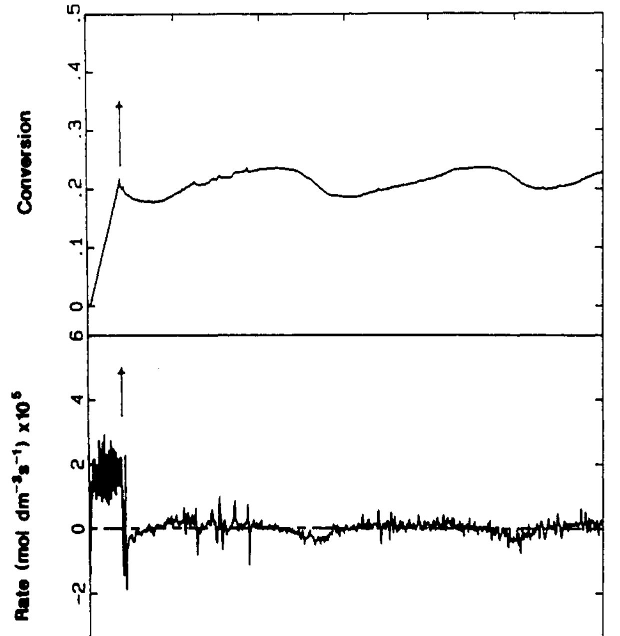

Figure 4. Conversion and polymerization rate for γ-radiolysis-initiated styrene polymerization in poly(propylene glycol) of MW 4000: T = 50 °C; [styrene] = 0.9 mol dm^{-3}; γ intensity = 82 krad h^{-1}. Arrow indicates the time of removal from the radiation source.

This behavior was independent of the conversion reached by the polymerization when the vessel was removed from the source. If there were a significant number of trapped macroradicals present upon removal from the source, one would expect instead the polymerization to continue at a rate equal to (or only slightly lower than) the rate observed in the source.

It is reasonable to attribute the observed fast drop in polymerization rate to the rapid reduction of the radical population by termination. Indeed, a rapid decrease in polymerization rate upon removal from a γ source has been observed in both styrene[20,28] and MMA[29] systems where radical annihilation is largely by termination, *even at very high conversion* when the monomer/polymer mix should be glassy, and hence when conditions should be ideal for the formation of trapped macroradicals.

It is now realized that the explanation for this (both qualitatively and quantitatively) in emulsion polymerization systems is "reaction/diffusion" or residual termination:[30] even in a glassy system, an entangled macroradical can diffuse by propagating. This leads to a termination rate that is comparatively rapid,[31] except at extremely high conversions (say, 99% polymer). Moreover, in a system such as the present one, where the silicone oil provides a highly viscous, but not glassy, environment, there is another mechanism which must lead to rapid radical annihilation: "short/long" termination.[28,32] This is termination between a short free radical, formed by transfer from a long one, diffusing rapidly until it undergoes termination with a relatively immobile (long) macroradical. Precise modeling of this effect can quantitatively explain all γ radiolysis relaxation data observed to date in styrene and MMA emulsion polymerization γ relaxation experiments.[32] Although the present system is a form of dispersion polymerization, and hence has only qualitative similarities to the emulsion polymerization experiments just discussed, the relaxation rates observed on removal from the source are similar in both systems. It therefore seems quite reasonable to posit the same general explanation (reaction/diffusion termination and/or short/long termination) for the rapid relaxation rates observed in the present system.

The final outcome of the present γ relaxation experiments is that polymerization ceases extremely rapidly upon removal from the source of free radicals, and moreover this result is quite reasonable on theoretical grounds. However, this result seems *irreconcilable with the trapped-radical hypothesis* used to infer the formation of the block copolymer in the viscous-solvent dispersion polymerization experimental procedure.

Experiment 4. The preceding three experiments appear to cast considerable doubt on the original interpretation of the experimental procedure for viscous-solvent dispersion polymerization: i.e., that the method results in extensive formation of block copolymer. Nevertheless, the first of the three types of experiments reported here ("Experiment 1") did in fact result in the formation of some type of copolymer. The purpose of this fourth set of experiments is to examine just what type of copolymer this might be.

HPLC/NMR analysis of the product of the first experiment suggests some copolymer species of blocky nature. Graft copolymers constitute the other type of polymer, which has properties similar to those of the block species: the block copolymers can in fact be regarded as a particular case of the graft family. The production of such species in the chemically initiated runs could be explained by the production of free radicals on the backbone of the homopolystyrene as a result of transfer reactions with primary free radicals generated by decomposition of the chemical initiator. Indeed, this type of mechanism is involved in the production of graft copolymer used in steric stabilization.[33] The following experiment was an attempt to check this hypothesis.

A total of 0.54 g of homopolystyrene produced in a previous experiment together with 0.02 g of AIBN was dissolved in 3.2 g of benzene. This solution was gently mixed with 8.5 g of PEG 400 for 2 h at 65 °C. A total of 1.3 g of MMA was then added to the vessel and allowed to react for 24 h at the same temperature. The reactor was then opened and the mixture poured into methanol. The HPLC chromatogram of the crude product showed the presence of a copolymer fraction containing about 30% of the polystyrene originally dispersed in the system.

Although qualitative, this last experiment clearly demonstrates that the formation of the graft copolymer cannot be excluded from the general scheme of a chemically initiated polymerization in which monomers are sequentially introduced in the reactor. That is, the copolymer observed using the experimental procedure of Seymour and co-workers could have resulted from such a grafting reaction, originating from any of the three possibilities discussed in the context of Experiment 2 to explain the origin of the residual free-radical production: residual initiator, thermal, or impurities.

Conclusion

The experimental results reported in this paper strongly indicate that the "trapped-macroradical" model developed to interpret the results of viscous-solvent dispersion polymerizations is incorrect, at least in the case of styrene. The present results imply instead that the observed initiation of the second monomer polymerization is due to residual primary radicals (which could arise from undecomposed initiator, from impurities, or from thermal initiation of monomer). When a totally controllable initiator system is used, regardless of the conversion reached, the polymerization rate decreases very rapidly on removal of the source of initiating free radicals (a result that is completely consistent with the findings in other dispersed systems that termination at high conversion is relatively rapid because of reaction/diffusion between two entangled macroradicals and/or a short free radical formed by transfer diffusing quickly to an entangled macroradical). This observation refutes the existence of any significant amount of trapped-macroradical activity. Viscous-solvent dispersion polymerizations, instead of producing block copolymer, probably form mixtures of graft and statistical copolymers, the former probably arising from a transfer mechanism.

In summary, this work refutes the trapped-macroradical model for styrene polymerization in viscous media: the results of several experiments are qualitatively different from those expected on the basis of this model. The approach used here had as its original aim the elucidation of the purported mechanism by carrying out experiments whose results should be predictable from the supposed mechanism; instead, it resulted in a refutation of that mechanism.

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