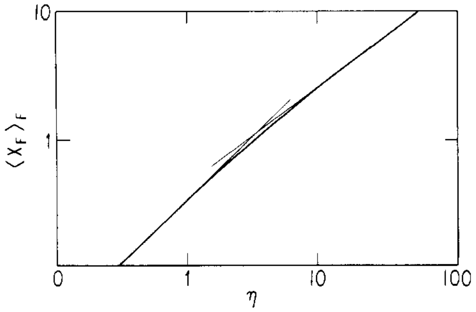

Figure 2. Plot of $\langle X_F\rangle_F$ vs. η in 3-space, where $\langle X_F\rangle_F = \langle \mathbf{R}\cdot\mathbf{F}\rangle_F/R_0|\mathbf{F}|$ and $\eta = |\mathbf{F}|R_0/kT$. Note that the crossover range is very wide.

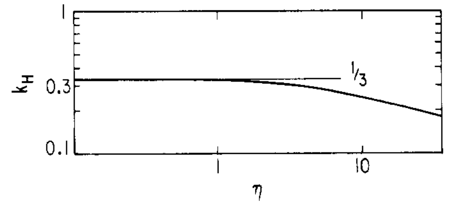

Figure 3. Plot of the effective Hooke constant $k_H = kT\langle \mathbf{R}\cdot\mathbf{F}\rangle_F/|\mathbf{F}|^2R_0^2$ vs. η in 3-space. k_H is $^1/_3$ in the weak-force limit. It deviates significantly from $^1/_3$ for $\eta \gtrsim 1$.

and is expected to be almost perfect if we extend our calculation to order ϵ^2. Even in 2-space ($\epsilon = 2$), eq 1 displays the correct qualitative features.

The distribution function (2) can be used to calculate the average of the component $R_F \equiv \langle \mathbf{R}\cdot\mathbf{F}\rangle_F/|\mathbf{F}|$ of $\mathbf{R}$ parallel to $\mathbf{F}$, where $\langle\ \rangle_F$ denotes the average over the ensemble $f(\mathbf{r})\exp(\beta\mathbf{F}\cdot\mathbf{R})$ with the external force $\mathbf{F}$ imposed. $X_F \equiv R_F/R_0$ is given as a function of $\eta = \beta|\mathbf{F}|R_0$ in Figure 2. The effective Hooke constant $k_H = kT\langle\mathbf{R}\cdot\mathbf{F}\rangle_F/|\mathbf{F}|^2R_0^2 \equiv \langle X_F\rangle_F/\eta$ is given in Figure 3. In the weak-force limit $\mathbf{F} \rightarrow \mathbf{0}$, $\exp(\beta\mathbf{F}\cdot\mathbf{R})$ is expanded in $\mathbf{F}$, and the result $k_H = 1/d$ in d-space follows directly from the spherical symmetry of the distribution function $f(\mathbf{r})$. Figures 2 and 3 show that Hooke's law is valid for $\eta \lesssim 0.8$. For $\eta \gtrsim 1$, there is a significant deviation from this linear law. The strongly stretched asymptote is reached at around $\eta \simeq 20$. The crossover region is thus very wide. If there are experimental errors or sampling errors in Monte Carlo calculations, then, as is seen from Figure 2 of ref 3, the crossover region is made to appear narrow, so that the crossover seems abrupt. Our calculation is to order ϵ, so the asymptotic slope for higher η in Figure 2 is 0.75 instead of the scaling result of ~0.66. However, the semiquantitative agreement with the Monte Carlo result is encouraging.

Acknowledgment. We are grateful to Dr. I. Webman for sending us a copy of his paper prior to publication. T.O. is also grateful to Professor D. Jasnow for his hospitality at the University of Pittsburgh. This research is supported, in part, by NSF Grants DMR78-26630 (Polymers Program) and DMR 76-19443.

References and Notes

(1) (a) The University of Chicago. (b) University of Pittsburgh. (c) On leave of absence from Kyushu University, Fukuoka, Japan.
(2) Pincus, P. *Macromolecules* **1976**, *9*, 386.
(3) Webman, I.; Lebowitz, J. L.; Kalos, M. M. *Phys. Rev. A* **1981**, *23*, 316.
(4) Oono, Y.; Ohta, T.; Freed, K. F. *J. Chem. Phys.*, in press.
(5) Domb, C.; Gillis, J.; Wilmers, G. *Proc. Phys. Soc. London* **1965**, *85*, 625.

Preparation of Homogeneous "Living" Polyvinyl Gels with Application to Solvent Purification

F. S. BATES and R. E. COHEN*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Received June 20, 1980

Introduction

In this paper we report on the polymerization of divinylbenzene (DVB) into homogeneous gels containing a significant concentration of residual vinyl groups. Methods are described whereby microsyneresis,[1] commonly observed in the polymerization of DVB, is eliminated. These methods of synthesis, therefore, place no restrictions on overall sample size and yield materials of substantial mechanical strength. The utility of these novel homogeneous polyvinyl macrogels is demonstrated in solvent purification.

Experimental Section

Materials. Divinylbenzene (Matheson Coleman and Bell, practical grade) was washed with 10% NaOH and with distilled water and was stored over molecular sieves at 0 °C. Proton NMR analysis confirmed a monomer composition of 60% DVB and 40% ethylstyrene (ES). The [*m*-DVB]/[*p*-DVB] was reported as 3:1 by the manufacturer. Reagent grade benzene, tetrahydrofuran (THF), 1,4-dioxane, and toluene were dried over molecular sieves. *n*- and *sec*-butyllithiums were diluted in hexane or used as received from Aldrich; concentrations were verified by titration, using the method of Eppley and Dixon.[2]

Gel Synthesis. Reactions were performed at room temperature in sealed, flamed, and argon-flushed Pyrex test tubes. Solvents and monomer were each introduced to the vessel by syringe and mixed. Addition of initiator was followed by a color change from colorless to burgundy brown and subsequent gelation. The reacting solution/gel was left for 24 h and recovered in benzene. During storage in benzene, slow reaction with oxygen terminated the living gels, as indicated by loss of color.

Gelation reactions were conducted in solution over a range of monomer concentrations from 2 to 40% (v/v) and at an initiator concentration of 0.016 M. Varying the [THF]/[I] molar ratio between 0 and 4 in benzene has a dramatic effect on the product obtained. Initiation in the absence of THF leads to slow development of color with subsequent polymerization and gelation dominated by extensive microsyneresis; the opaque gel so produced has little mechanical strength and crumbles upon handling. Addition of initiator to a solution with [THF]/[I] = 4 instantaneously produces a burgundy color followed by rapid homogeneous gelation. The product is a clear uniform gel of superior strength. Varying [THF]/[I] between 0 and 4 results in large changes in reaction time and product characteristics. A value of [THF]/[I] = 4 provides adequate time for mixing prior to gelation and yields a product suitable for application to solvent purification (see below). This gel can be readily cut into serviceable pieces as recovered in the swollen state while also containing a significant concentration of accessible vinyl groups. The conditions for the synthesis of this gel are summarized in Table I. As described in the Discussion, homogeneous gels were also obtained from reactions carried out in a mixed solvent composed of 75% dioxane and 25% toluene (v/v).

Characterization. The gel of Table I was analyzed for accessible vinyl content in the following manner: 1.5 g (dry weight) of 0.5-cm^3-size swollen particles was suspended in toluene, charged with excess *n*-BuLi, and allowed to react under purified argon for 1 week. The presence of available vinyl groups in the gels was evidenced by the appearance of a deep reddish brown color. The solution was then drained and a 250-mL aliquot of a standardized solution of toluene and benzoic acid was added. The activated gel particles turned colorless. Aliquots (50 mL each) of the remaining solution were titrated for benzoic acid content with a standardized solution of methanol and sodium methoxide. Phenophthalein was added as an end point indicator. The titration technique was verified independently on a known solution of benzoic acid in toluene. This method yielded a value of 1.4

0024-9297/81/2214-0881$01.25/0 © 1981 American Chemical Society

Table I
Experimental Conditions for the Synthesis of Gels Used in Solvent Purification

reagent	concn, M
DVB (75% meta, 25% para)	0.83
ethylstyrene (mixed isomers)	0.55
benzene	9.01
n-BuLi	0.016
THF	0.064

× 10^{-3} mol of available vinyl groups per gram of dry gel.

The method of characterization was chosen in order to duplicate conditions employed during solvent purification, as discussed in the following section. Presumably the true vinyl content is considerably higher since this chemical reaction is expected to be diffusion limited and because reaction of more than one vinyl group per initiator molecule is possible.

Application. The polyvinyl gel was tested for solvent purification capabilities in a series of anionic polymerizations. Approximately 2.0 g (dry weight) of gel was suspended over 2000 mL of distilled solvent under argon. For the case of polymerizations to be later initiated with *n*-butyllithium, a suitable amount of anisole was added to the solvent to provide for a high rate of initiation.[3]

Sufficient *n*-BuLi (1.6 M) was added to the impure solvent and the solution was stirred for several days. Sequential lowering of clear gel particles into this solvent provided fresh vinyl material for excess initiator removal as evidenced by the appearance of a reddish brown color in the gel. When the newly added gel particles remained colorless, the purification of the solvent was assumed to be complete. Gas chromatographic analysis was used to confirm the purity of the gel-treated solvent; the absence of DVB at a sensitivity of 1 ppm was verified. The purity of the solvent was also verified through its use in various anionic polymerizations as discussed below.

Styrene and butadiene monomers were purified by conventional methods.[4,5] Diluted solutions of *n*- and *sec*-butyllithiums in hexane were titrated as previously mentioned.[2] All polymerizations were carried out under purified argon.

After the purified solvent was admitted to the reactor, leaving the activated gels behind, a metered amount of monomer was added and initiated with butyllithium. The amount of monomer varied between 33 and 100 g to achieve a level of about 5% (by volume) of the reaction medium. Reaction temperatures ranged from 30 to 50 °C. Upon completion of the reaction, the "living" polymer was terminated with a small amount of methanol.

The polymers were analyzed by high-performance size exclusion chromatography (HPSEC),[6] employing a set of Zorbax PSM bimodal columns with THF as the mobile phase. Table II compares the experimentally obtained number-average molecular weight of each sample to that expected from the stoichiometry of initiator and monomer. Deviations of actual to theoretical molecular weight are well within the limitations set by the accuracy of our equipment. Low polydispersity indices were also obtained as expected and are listed in Table II.

A polymerization under similar conditions with solvent prepared in an identical fashion except for the gel purification resulted in complete deactivation of the calculated quantity of initiator and no polymerization. This clearly illustrates the capabilities of the polyvinyl gel material in this solvent purification application.

It should also be noted that the counterion utilized in solvent purification can be matched with that used during polymer synthesis, thereby eliminating difficulties which might arise due to counterion exchange. Another potential complication of this method of solvent purification is the presence of products of the reaction between initiator and impurities in the solvents. Under many conditions (diene polymerization being one possible exception) such byproducts have no detrimental influence on the polymerization. Furthermore, sufficient gel activation should provide an adequate number of "living" sites to bind these complexing compounds, which otherwise would be destined to remain in solution. However, to test the possible influence of these byproducts, NMR analysis of the polybutadiene sample listed in Table II was carried out. This experiment identified a microstructure composed of 87% 1,4 (cis and trans) and 13% 1,2 addition. This is consistent with previously documented values for lithium-catalyzed anionic polybutadiene prepared in nonpolar solvents, using conventional methods of solvent purification.[5]

Table II
Comparison of Theoretical and Actual Molecular Weights Obtained for Polymerization of Listed Monomers in Solvent Purified Using Polyvinyl Gels

monomer	solvent	M_n(theor)[a]	M_n(exptl)[b]	M_w/M_n[b]
styrene	toluene[c]	99 000	105 000	1.19[d]
styrene	benzene[e]	81 000	81 000	1.07
styrene	benzene[e]	149 000	144 000	1.06
styrene	benzene[e]	400 000	440 000	1.06
styrene	benzene[e]	440 000	430 000	1.06
butadiene	benzene[e]	90 000	94 000[f]	1.05[f]

[a] Determined by stoichiometry of monomer and initiator charged to the reactor. [b] Determined by HPSEC calibrated with 10 polystyrene standards. [c] Initiated with *sec*-butyllithium. [d] This relatively high value is expected due to chain transfer reaction.[13] [e] Initiated with *n*-butyllithium in the presence of anisole. [f] Calculated by using universal calibration with data from ref 14.

Discussion

The unfavorable structural characteristics of DVB gels prepared by anionic polymerizations in benzene can be attributed to microsyneresis. An analogous situation develops when DVB is emulsion polymerized, although the product is recovered as a microgel.[10] Chemical and physical applications of such materials are limited to a "microregime", e.g., as multifunctional initiators for star polymers,[7-9] in paint formulations[10] or as column packing for gel permeation chromatography. Addition of THF to benzene at a molar concentration four times that of initiator suppresses microsyneresis, permitting the synthesis of macroscopically homogeneous gels. The following discussion addresses the underlying chemical mechanism by which microsyneresis is believed to be avoided.

We have observed that substitution of sec-butyllithium for *n*-butyllithium in the absence of THF decreases the time to gelation but does not, by itself, suppress the undesirable microsyneresis. Addition of THF also increases the rate of initiation and thus also decreases gelation times. However, in view of the results obtained with *sec*- and *n*-butyllithiums in the absence of THF, the major contribution of THF in suppressing syneresis in the gelation reactions must be attributed to something other than rapid initiation.

We assume that the mechanisms of vinyl addition to lithium polystyryl and lithium poly(divinylbenzyl) are identical, based on the reported similarity between the reaction kinetics of each in benzene and in benzene/THF.[11,12] It is well established that lithium polystyryl exists primarily in the dimeric form in benzene, although vinyl addition proceeds predominantly via dissociated contact ion pairs.[5] The presence of THF has two significant effects on lithium polystyryl in benzene. First, it eliminates ion pair associations; unassociated lithium polystyryl etherates are the predominant living species in solution. Second, the mechanism of propagation in the presence of THF is dramatically changed so that vinyl addition occurs via a coordinated vinyl–etherate complex.[5] We believe that it is the first of these two effects which leads to the suppression of microsyneresis in our gelation reactions.

In order to test this hypothesis, we performed a series of gelation reactions in a mixed solvent composed of 75% dioxane and 25% toluene (v/v). It has been shown that lithium polystyryl in dioxane exists as and propagates via

Table III
Variations Observed in Gelation Reactions and Products[a]

solvent	benzene	benzene/THF (0.994/0.006)	dioxane/toluene (0.750/0.250)
time to full color, s	>120	instantaneous	instantaneous
time to gel,[b] s	~1200	~20	~160
expected overall rate constant,[c] L mol^{-1} s^{-1}	0.01	25.3[d]	0.9
clarity of gel	opaque	clear	clear
structural characteristics of gel	inhomogeneous (powder)	homogeneous (swollen rubber)	homogeneous (swollen rubber)

[a] Experimental conditions are as in Table I, keeping the relative volume of solvent constant. [b] Subject to small deviations due to an inability to accurately control reaction temperature. [c] Based on values for lithium polystyryl (from ref 5). [d] Assuming propagation is via monoetherate of lithium polystyryl (from ref 5).

unassociated contact ion pairs.[5] Therefore by carrying out a gelation in this solvent, we have maintained the same addition mechanism as for the case of reaction in pure benzene solvent, while essentially eliminating living-end association. The 25% toluene was added to the dioxane in order to obtain a solubility parameter comparable to that of benzene while having the dielectric characteristics of the solvent mixture for the most part unchanged from that of pure dioxane. The results of these experiments appear in Table III along with analogous information from the previous two solvent systems. The clarity and structural characteristics of the dioxane/toluene and benzene/THF gels were indistinguishable. The gelation times for the three cases are consistent with the reported values for the rates of polymerization of styrene in the respective solvents (Table III). This supports our earlier assumption regarding the similarity in reaction mechanism between styrene and divinylbenzene in each system.

In the case of dimeric lithium poly(divinylbenzyl), as found in benzene without THF, the proximity of the terminal pendent vinyl group of one living chain to the active end of its associated counterpart greatly enhances the probability of interchain reaction. Such reaction essentially doubles the molecular weight and the "living" functionality of the resulting species. Successive dimerization and cross-linking of separate species quickly increases the molecular weight, cross-link density, and "living" functionality of the growing polymer, which all lead to microsyneresis. Adding THF to benzene or using dioxane–toluene eliminates lithium poly(divinylbenzyl) dimerization. In the absence of such association early stage polymerization is expected to be predominantly linear chain growth due to the high concentration of monomer units relative to polymer repeat units. Linear polymerization is also enhanced by a factor of 2 for the vinyl content of DVB monomer compared to polymer repeat unit and by the inability of ethylstyrene to contribute to cross-linking. Prior to gelation, the reaction medium is composed of soluble living polymer which then forms a macroscopic homogeneous network.

The termination-free nature of this polymerization and high ceiling temperature ensure virtually complete incorporation of monomer into the gel. We have also observed that the gelation reaction stops at the point of swelling equilibrium; i.e., the "living" gel does not undergo macrosyneresis[1] nor does the recovered product swell further in excess solvent. Future work will be aimed at clarifying this phenomenon, the kinetics of the homogeneous gelation reactions, and the detailed structural features of the products.

Conclusions

A method has been presented for preparing homogeneous gels of divinylbenzene–ethylstyrene which contain a significant concentration of pendant vinyl groups. Microsyneresis is avoided by adding a suitable amount of THF to the reaction medium, thereby eliminating unwanted living-end association.

The utility of these gels has been demonstrated for the particular case of purification of solvent. Numerous other applications can be envisioned which exploit the variety of organic and organometallic reactions to which the pendant vinyl group is susceptible, e.g., use as a catalyst substrate.

Acknowledgment. This work has been supported in part by the Office of Naval Research. We gratefully acknowledge very helpful discussions with C. Schwier.

References and Notes

(1) Dusek, K. "Polymer Networks—Structure and Mechanical Properties"; Chompff, A. J., Newman, S., Eds.; Plenum Press: New York, 1971; p 245.
(2) Eppley, R. L.; Dixon, J. A. *J. Organomet. Chem.* **1967**, *8*, 176.
(3) Ceresa, R. J., Ed. "Block and Graft Copolymerization"; Wiley: New York, 1973; Vol. 1.
(4) Weiss, P.; Hild, G.; Henry, J.; Rempp, P. *Makromol. Chem.* **1970**, *135*, 249.
(5) Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Processes"; Interscience: New York, 1968.
(6) Yau, W. W.; Ginnard, C. R.; Kirkland, J. J. *J. Chromatogr.* **1978**, *149*, 465.
(7) Eschwey, H.; Hallensleben, M.; Burchard, W. *Makromol. Chem.* **1973**, *173*, 235.
(8) Eschwey, M.; Burchard, W. *Polymer* **1975**, *16*, 180.
(9) Eschwey, M.; Burchard, W. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 53*.
(10) Funke, W. *J. Oil Colour Chem. Assoc.* **1977**, *60*, 483.
(11) Worsfold, D. J. *Macromolecules* **1970**, *3*, 514.
(12) Worsfold, D. J.; Zilliox, J. G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379.
(13) Gatzke, A. L. *J. Polym. Sci., Part A-1* **1969**, *7*, 2281.
(14) Evans, J. M. *Polym. Eng. Sci.* **1973**, *13*, 6.

Carbon-13 Nuclear Magnetic Resonance Spectra of Alternating and Random Copolymers of Methyl Acrylate with Styrene

H. KOINUMA,* T. TANABE, and H. HIRAI

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. *Received September 30, 1980*

In spite of the wide applicability of NMR spectroscopy for structural elucidation of polymers, spectral patterns of copolymers are frequently too complicated, owing to both configurational (tacticity) and compositional (monomer sequence) distributions, to provide us with quantitative information concerning the microstructure. Recently we showed that the alternating copolymer could

0024-9297/81/2214-0883$01.25/0 © 1981 American Chemical Society