Anionic polymerization and polymer properties of 2-isopropenylnaphthalene and 2-vinylnaphthalene

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(*Received 12 October 1991; revised 2 March 1992; accepted 5 March 1992*)

2-Isopropenylnaphthalene (2-IPN) and 2-vinylnaphthalene (2-VN) were polymerized in toluene with sec-butyllithium initiator. For 2-IPN, equilibrium monomer concentrations were determined, as well as the enthalpy, entropy and 'absolute' ceiling temperature, for its polymerization. Densities of both polymers were measured and their solubility parameters were calculated. They are, respectively, for 2-IPN, $1.105\,\mathrm{g\,cm^{-3}}$ and $9.2\,\mathrm{cal^{1/2}\,cm^{-3/2}}$, and for 2-VN, $1.108\,\mathrm{g\,cm^{-3}}$ and $9.4\,\mathrm{cal^{1/2}\,cm^{-3/2}}$.

(Keywords: anionic polymerization; 2-vinylnaphthalene; 2-isopropenylnaphthalene)

INTRODUCTION

The anionic polymerization of 2-isopropenylnaphthalene (2-IPN) has received some attention in recent years, but scant data have been reported on the anionic polymerization of 2-vinylnaphthalene (2-VN)[1–8]. In all of these studies, tetrahydrofuran was used as the polymerization solvent, with sodium or potassium as the counterion.

In addition, 2-IPN, like all isopropenyl aryl monomers, undergoes equilibrium polymerization except at very low temperatures. Equilibrium monomer concentrations, $[\mathrm{M}]_e$, as a function of polymerization temperature have been reported for 2-IPN only in tetrahydrofuran[8]. However, solvent effects are known for anionic equilibrium polymerizations[9–12].

Hence it was of interest to: (1) polymerize both of these monomers in a hydrocarbon solvent with a lithium counterion; (2) measure some properties of the resultant polymers; and (3) determine $[\mathrm{M}]_e$ as a function of temperature for 2-IPN polymerized under these reaction conditions.

EXPERIMENTAL

Materials

2-Vinylnaphthalene was obtained from the Aldrich Chemical Company as a tan solid. As received it required excessive levels of sec-butyllithium to initiate its polymerization in toluene, i.e. it had a very high scavenger level. Purification by distillation under nitrogen *in vacuo* (b.p. 77°C at $\sim 10^2$ Pa) gave a white solid which initiated readily.

2-Isopropenylnaphthalene was prepared by alkylating naphthalene with propylene by the Process Engineering Research Division in these laboratories, followed by dehydrogenation. The product was distilled under nitrogen *in vacuo* (b.p. = 87–88°C at $\sim 0.8 \times 10^2$ Pa). Its melting point was 54°C, and its density was $1.052\,\mathrm{g\,cm^{-3}}$ at 23°C. The purity determined by vapour phase chromatography was >99%.

Solvents. Toluene was reagent grade. Diethyl ether was ACS reagent grade. Both were stored under nitrogen over molecular sieves, and transferred by syringe.

Initiator. A 1.44 M solution of sec-butyllithium from Aldrich Chemical Company was used as received for 2-VN polymerizations. For 2-IPN polymerizations, it was diluted to 1.00 M with purified cyclohexane. All initiator solutions were analysed by the Gilman–Cartledge method[13]. Diethyl ether when used as a polar modifier for 2-IPN polymerization was utilized as a 2.0 M solution in cyclohexane.

Polymerizations

2-Vinylnaphthalene. A 2.2 M solution of distilled 2-VN was prepared in reagent grade toluene and passed through a water-cooled silica gel column; 20 ml portions were collected in 28 g screw-capped bottles. Caps were lined with a self-sealing rubber gasket, and a Teflon gasket facing the solution. All operations were done under nitrogen.

A 1.44 M solution of sec-butyllithium in cyclohexane was syringed dropwise into the 2-VN solution until a permanent rose colour formed. This typically required two drops of sec-butyllithium solution. Then the requisite amount of the initiator solution, calculated to produce the desired molecular weight of poly(2-VN), was added. A dark red colour formed at once, and the bottle became warm. It was placed in a cold water bath for 1 h to moderate the reaction, then stored for at least 18 h at 5°C to ensure complete polymerization of the 2-VN.

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0032-3861/92/235073-03

2-Isopropenylnaphthalene. It was found in the preliminary study of 2-IPN polymerization in cyclohexane solvent with this initiator system that poly(2-IPN) precipitated. This observation has also been made by Hsieh and Wang[7]. Thus toluene was chosen as the solvent for this work. A 2.54 M solution of 2-IPN in toluene was prepared and passed through a water-cooled silica gel column; 35 ml portions were collected in 56 g screw-capped bottles which were sealed as described above. All operations were done under nitrogen. There is a slight preferential absorption of 2-IPN on the silica gel; hence the treated solutions were analysed by vapour phase chromatography. Since 2-IPN is a solid at ambient temperature, analyses could also be checked by careful evaporation of aliquots of the solutions. All analyses showed the solutions were 2.52 M ($\pm<1.0\%$) in 2-IPN.

Polymerizations were carried out in a manner described previously[12]. Under a nitrogen blanket, 10.0 ml of the 2-IPN solution was syringed into a 28 g screw-capped bottle, sealed as described above. Then 0.15 ml of 2.0 M diethyl ether was syringed into the bottle. Impurities in the solution were scavenged by syringing 1.0 M sec-butyllithium dropwise into the solution until a faint colour persisted. This usually required 0.03 ml of the sec-butyllithium solution. Then 0.15 ml of the sec-butyllithium solution was added, producing a lithium concentration of 0.0145 M, and a molar ratio of ether/Li $=2.0$. This ether/Li ratio was chosen since it produces rapid initiation of the polymerization, and also accelerates the polymerization rate, which permits relatively rapid attainment of equilibrium conditions. At this low ether/Li ratio, the presence of the polar modifier does not appear[12] to affect the values of $[M]_e$.

A dark greenish-black colour formed at once. The bottle was quickly suspended in a Lauda constant temperature bath, controlled at the desired temperature to ± 0.02°C. Polymerizations were run for at least 48 h, and usually for 72 h.

Termination and polymer isolation. Polymerizations were terminated with a drop of deaerated methanol, and solutions were coagulated in methanol containing a phenolic antioxidant. These mixtures were stored for 24 h, and the precipitated polymers were filtered and washed repeatedly with methanol. They were then dried *in vacuo* at <90°C to constant weight.

Determination of $[M]_e$ for IPN. The $[M]_e$ values were calculated as usual, correcting for monomer concentration change due to dilution by the initiator solutions, and for volume contraction of the solution that occurs during polymerization[12,14].

Polymer properties

Poly(2-VN). Polymers were compression moulded at 204°C in a ~5.1 × ~2.5 × ~0.1 cm cavity and the moulds were cooled under pressure. Density was determined on three void-free samples by the buoyancy method, using a Mettler AE163 electronic balance with deionized water as the reference liquid. Their densities, determined at 25°C, were 1.108, 1.108 and 1.107 $\mathrm{g\,cm^{-3}}$.

Poly(2-IPN). Density was determined in the same manner as for poly(2-VN), except that samples were prepared by casting a moderately thick film from methylene chloride. It was air-dried for several days, then dried *in vacuo* at ambient temperature to constant weight.

For all polymers, glass transition temperatures (T_gs) were determined by both d.s.c. and t.m.a. Analyses by g.p.c. showed that all polymers had very narrow molecular weight distributions.

RESULTS AND DISCUSSION

Polymerization

2-Vinylnaphthalene. Rate studies were not carried out for polymerizations of this monomer but qualitatively 2-VN appears to polymerize similarly to styrene in an anionic system. Heat evolution and increase in the viscosities of the solutions indicated polymerizations were rapid, and polymer yields were quantitative. Although the colour of the 2-VN anion in tetrahydrofuran has been reported as green[1,2], in toluene it is a deep red, similar to the styryl anion.

2-Isopropenylnaphthalene. The equilibrium polymerization of this monomer was studied in detail. The $[M]_e$ values found at various temperatures are given in *Table 1*. The relation between temperature and $[M]_e$ has been defined by Dainton and Ivin[15] as:

$$T_c=\frac{\Delta H^0}{\Delta S^0+R\ln[M]_e}$$

where T_c is the ceiling temperature corresponding to a given $[M]_e$. This equation indicates that $\ln[M]_e$ should be a linear function of $1/T_c$, which was confirmed for the anionic polymerization of 2-IPN in tetrahydrofuran by Hopff and Lussi[8]. The data of *Table 1* were so plotted in *Figure 1*, showing the linear relation between the parameters for this polymerization in toluene. The data of Hopff and Lussi are also plotted for comparison. The $[M]_e$ values were slightly lower for polymerization in toluene than in the polar solvent tetrahydrofuran. These results parallel findings for polymerization of a-methylstyrene in polar and non-polar solvents[9–12].

The data of *Table 1* and *Figure 1* were used to calculate the entropy and enthalpy of the polymerization. These are, respectively, $-29.9\,\mathrm{cal\,mol^{-1}\,°C^{-1}}$ and $-9.0\,\mathrm{kcal\,mol^{-1}}$ compared to $-39.0\,\mathrm{cal\,mol^{-1}\,°C^{-1}}$ and $-11.4\,\mathrm{kcal\,mol^{-1}}$ for a-methylstyrene polymerized in cyclohexane[12].

The plots in *Figure 1* were extrapolated to the concentration of neat 2-IPN, where solvent effects should disappear. This is represented by the line extending from the ordinate. From the data found in toluene, the T_c for neat 2-IPN is 69°C, and from that found in tetrahydrofuran, 68°C. These values are in very good agreement, and may be considered to be within the margin of experimental error. This is the 'absolute' T_c for 2-IPN, above which it cannot be polymerized to high molecular weight polymer. It can be noted that the 'absolute' T_c of 2-IPN is 15°C higher than that of a-methylstyrene[12].

Table 1 Equilibrium monomer concentrations

T (°C)	$[M]_e$ (mol l^{-1})
−5	0.17
5	0.31
15	0.53
25	0.96

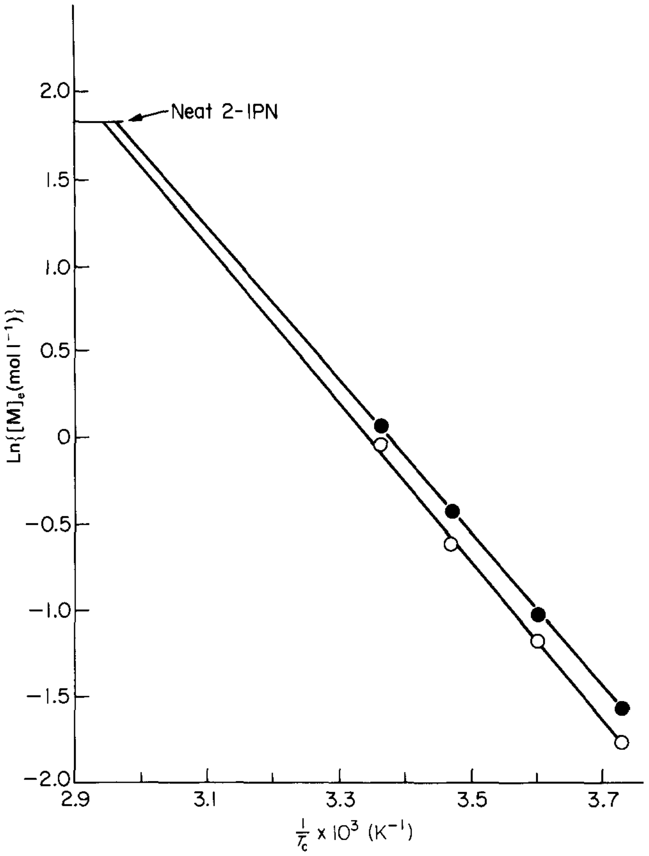

Figure 1 Natural logarithm of the equilibrium monomer concentration ln$[M]_e$, as a function of the inverse of the ceiling temperature, $1/T_c$: (○) toluene; (●) tetrahydrofuran

Table 2 Glass transition temperature of poly(2-VN)

Molecular weight	T_g (°C)
20 000	137
30 000	145
49 000	147[3]

Table 3 Solubility parameters of polyaryls

Polymer	Density (g cm^{-3})	Solubility parameter[a] (cal$^{1/2}$ cm$^{-3/2}$)
Polystyrene	1.05	9.0
Poly(a-methylstyrene)	1.069	9.0
Poly(2-isopropenylnaphthalene)	1.105	9.2
Poly(2-vinylnaphthalene)	1.108	9.4

[a] After Small[16]

Glass transition temperature

2-Vinylnaphthalene. The T_gs of poly(2-VN) at two molecular weights, prepared in this study, are given in *Table 2*, together with a result reported by Utracki and Simha[3]. They reported that the limiting T_g of poly(2-VN) at very high molecular weight is 151°C.

2-Isopropenylnaphthalene. The T_g of two separate samples of poly(2-IPN), with molecular weights of ~20 000, was 208°C. This agrees very closely with the data of Engel and Schulz[4]. At this molecular weight, polystyrene and poly(a-methylstyrene) have T_gs of 90 and 155°C, respectively.

Solubility parameters

From the densities of the polymers, their solubility parameters were calculated, using the method of Small[16]. The results are given in *Table 3*, together with those of polystyrene and poly(a-methylstyrene) for comparison.

Poly(2-IPN) has a solubility parameter that is slightly but significantly higher than that of polystyrene. This is probably the reason that poly(2-IPN) is insoluble in cyclohexane, and indicates that poly(2-IPN) should undergo stronger phase separation than polystyrene or poly(a-methylstyrene) in block copolymers with polydienes.

Poly(2-VN) has the highest solubility parameter (9.4) of the four polyaryls that have been studied in these laboratories. This value indicates that it should undergo very strong phase separation in block copolymers with polydienes.

Both the T_gs and the solubility parameters of poly(2-IPN) and poly(2-VN) suggest that they should form ABA-type triblock thermoplastic elastomers with polydienes, which might have exceptional stress–strain properties. In particular, they might be expected to have improved tensile strengths in the range of 20–100°C, compared to similar block copolymers based on polystyrene or poly(a-methylstyrene).

ACKNOWLEDGEMENTS

The authors wish to thank the Goodyear Tire & Rubber Company for permission to publish this work. The T_g determinations were done by R. S. Bell and the late W. Jaber. Dr G. S. Fielding-Russell provided helpful discussions on the calculation of solubility parameters by Small's method. This is contribution number 673 from the Research Laboratories of The Goodyear Tire & Rubber Company.

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