Notes to the Editor

Polymerization and copolymerization of vinylferrocene in the presence of lithium and n-butyllithium

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INTRODUCTION

Although vinylferrocene has been polymerized cationically, anionically and using soluble Ziegler–Natta catalysts, the majority of research has been concerned with free radical polymerizations. Whilst early studies on this monomer tended to regard it as an analogue of styrene, more recent studies suggest that it is quite distinct, mainly because of participation of the ferrocene nucleus in the polymerization reactions of the olefinic double bond. For example, in radical polymerizations in benzene, the growing polyvinylferrocene radical is terminated by an electron transfer reaction from a ferrocene nucleus in the chain[1,2]. In chloroform and other halogenated solvents a redox reaction between the ferrocene nucleus and the solvent produces radicals which initiate polymerization of the vinyl group[3]. Similarly, in spite of the enhanced reactivity of vinylferrocene towards electrophiles, cationic polymerization of this monomer does not occur at –78°C and only low molecular weight polymer is formed at 0°C. Because of the powerful electron releasing effect of the ferrocene group the olefinic double bond is electron rich[5,6], however, anionic polymerization occurs in the presence of n-butyllithium and methyllithium[7]. Since anionic polymerization is a convenient way to prepare block copolymers, the anionic polymerization of vinylferrocene has been examined.

EXPERIMENTAL

Vinylferrocene (ROC/RIC Chem. Corp. California) was purified as described previously[1–3]. Tetrahydrofuran was refluxed over sodium naphthalene for 6 h and then fractionally distilled from fresh sodium naphthalene, degassed and stored over sodium wire prior to use. Benzene was dried over calcium hydride fractionally distilled from n-butyllithium degassed and fractions distilled out as required. Isoprene (BDH Ltd, Poole) was degassed and stirred with calcium hydride for 24 h, fractionally distilled, exposed to n-butyllithium for 15 min and then collected in sealed ampoules and stored at –10°C. Research grade butadiene 99.9% purity (Cambrian Chemicals Ltd, Croydon) was dried over molecular sieves before use. 1,6-Dibromohexane (Koch-Light Ltd, Colnbrook) was dried over molecular sieves, fractionally distilled under reduced pressure and the middle fraction collected. n-Butyllithium (Koch-Light Ltd, Colnbrook) was used as clear 15% solutions in hexane. Lithium metal (BDH Ltd, Poole) supplied as 0.8 cm diameter rods was washed in ether and cut into sections 0.2 cm thick prior to use.

Homopolymerizations and copolymerizations of vinylferrocene using n-butyllithium were performed in sealed glass vessels after degassing all reactants at 10^{-4}mmHg using standard vacuum line techniques. When lithium metal was used as initiator, monomers and solvents were degassed on the vacuum line in a 250 cm^3 round-bottomed flask, lithium added under nitrogen and the reactions carried out as described elsewhere[8].

The absorption spectrum of the ion produced by the addition of butyllithium to vinylferrocene was determined by using a reaction vessel to which was attached an ampoule of butyllithium in hexane and a silica cell of 0.1 cm pathlength. A few milligrams of vinylferrocene were introduced into the reactor which was then evacuated. Tetrahydrofuran was distilled in, the vessel was sealed, and the butyllithium introduced by shattering the breakseal. The spectrum recorded after mixing is shown in *Figure 1* and consisted of a band at 390 nm, the spectrum of vinylferrocene monomer is included for comparison. The intensity of the absorption decreased with time and was no longer detectable after about 10 min. During this period, the solution became cloudy because of the formation of a precipitate. As expected for an anion, the absorption band at 390 nm disappeared immediately on the addition of methanol.

The polymers were isolated by precipitation into methanol and purified and characterized as described previously[1,2]. In some reactions an inorganic non-polymeric product, insoluble in benzene, was obtained which was separated from the polymer before precipitation into methanol.

RESULTS AND DISCUSSION

Homopolymerization

Vinylferrocene was found to homopolymerize fairly readily in the presence of lithium or n-butyllithium. In general, the percentage conversions of monomer to polymer were not high as shown in *Table 1*. Some of the polymeric products were not completely precipitated by methanol because of their low molecular weights. The benzene-soluble polymers separated from reactions of vinylferrocene in the presence of lithium or n-butyllithium

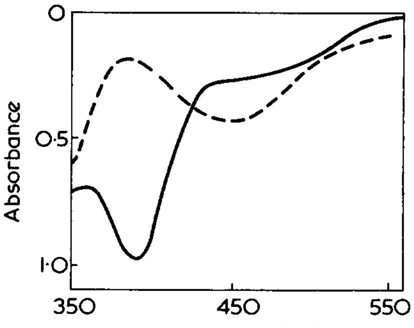

Figure 1 Absorption spectrum of the ion produced on adding butyllithium to vinylferrocene. — — —, spectrum of vinylferrocene

Table 1 Homopolymerization of vinylferrocene in the presence of lithium and n-butyllithium. $[M]_0 = 0.5$ mol/dm^3

Initiator (mol/dm)	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Fe (%)	$\bar{M}_n$
Li 0.5	THF	–78	3	10	23	4000
Li 0.5	THF/ethanol*	–10	3	1	–	–
Li 0.1	THF	–10	3	2	–	–
BuLi 0.02	Benzene	21	6	3	–	–
BuLi 0.05	Benzene	21	24	2	–	–
BuLi 0.02	Benzene/THF*	21	6	12	26	1400
BuLi 0.02	THF	–78	6	20	24	2800

* 100:2 v/v

Table 2 Copolymerization of vinylferrocene (M_1) in the presence of lithium (0.5 mol/dm^3) and n-butyllithium (0.02 mol/dm^3) in THF. Total monomer concentration – 0.5 mol/dm^3

Initiator	Comonomer (M_2)	M_1/M_2	Temperature (°C)	Time (h)	Conversion (%)	Fe (%)	T_g (°C)	$\bar{M}_n$
BuLi	Isoprene	1/20	23	3	27	1.1	–60	10 500
BuLi	Butadiene	2/1	–78	6	3	3.4	–40	3000
Li	1,6-Dibromohexane	2/1	–10	3	10	18.1	12	600
Li	1,6-Dibromohexane	2/1	–78	3	2	–	–	–

had similar i.r. and u.v. spectra to those prepared radically or cationically.

The iron contents tended to be low in those polymers prepared in the presence of lithium and the polymers isolated from these reactions produced broad n.m.r. spectra. Similar broadening in the n.m.r. spectra of polyvinylferrocene has previously been observed in polymers produced by radical polymerization$^{1-3}$.

The less than quantitative yields suggest that the polymerization of vinylferrocene involves a termination reaction, a conclusion supported by the formation of a precipitate and by the spectral studies. The heterogeneity which develops in the solution is probably due to some side reactions. The presence of side reactions is not unexpected since the parent compound, ferrocene, will react with lithium and its alkyls[9]. However, in the conditions used for polymerization no reaction was observed between ferrocene and lithium. For example, stirring ferrocene and lithium metal in THF at –10°C produced no reaction in 40 h and the starting materials were recovered in quantitative yield. Under the same conditions with vinylferrocene and lithium, the metal surface became tarnished and pitted and a brown solid was precipitated within 10 min suggesting that vinylferrocene is extremely prone to side reactions in this system. The amount of precipitate increased with time and elemental analysis showed it to contain C,H,Fe and Li in varying proportions dependent upon the reaction conditions. These complex, non-polymeric by-products were insoluble in all organic solvents and their i.r. spectra were completely devoid of the characteristic ferrocene absorptions.

Copolymerization

Although inorganic complexes were also formed in copolymerization reactions, copolymers were obtained with isoprene and butadiene in the presence of n-butyllithium and with 1,6-dibromohexane in the presence of lithium. Typical results are shown in *Table 2*.

The small amounts of iron incorporated into copolymers with isoprene and butadiene suggest that vinylferrocene is much less reactive than these dienes in anionic polymerizations. The copolymer of isoprene and vinylferrocene is interesting since these monomers do not appear to copolymerize with free radicals[10]. An attempt was made to generate a block copolymer by adding vinylferrocene to 'living' polyisoprenyl lithium in benzene. As in the case of the reaction of vinylferrocene with butyllithium, a brown precipitate was formed in a few minutes, but analysis of the polymer showed the presence of a few units of vinylferrocene per chain.

The copolymers with isoprene and butadiene were soft brown gums which eventually crosslinked in air. The isoprene copolymer appeared to become less viscous on storing initially which might suggest some decomposition reaction possibly catalysed by ferrocene. The copolymer with 1,6-dibromohexane was also a brown sticky gum but was completely stable in air since it contains no unsaturation. The infra-red spectrum as expected was similar to polyvinylferrocene except the absorptions at 2800 cm^{-1} of the methylene group were enhanced. It also exhibited a strong absorption 720 cm^{-1} which can be ascribed to the $-(-CH_2-)_6-$ methylene chain. Attempts to analyse the structure by n.m.r. spectroscopy were unsuccessful due to pronounced paramagnetic broadening.

The results show that vinylferrocene undergoes homo- and copolymerization in the presence of lithium and n-butyllithium in agreement with the results of Fitzgerald[7]. Although the system is complicated by side reactions between the ferrocene nucleus and the initiators, the polymerization appears to occur by an anionic mechanism. However, because of these side reactions the polymerization is inefficient and wasteful of monomer. With regard to initiation by lithium, polymerization can occur by anionic and/or radical mechanisms dependent upon the system[11]. Since vinylferrocene is polymerized by lithium in the presence of ethanol (see *Table 1*), it is possible that a radical mechanism is operative in this case. A radical propagation followed by an 'intralectran' termination would explain the broad n.m.r. spectra of these polymers$^{1-3}$. However, considerable more work is required to establish an unequivocal mechanism in these systems.

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