

Chain Transfer in the Anionic Polymerisation of Styrene

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THE anionic polymerisation of styrene at -78° is known to proceed in a number of solvents without chain transfer.¹ Also, when lithium is the counter-ion no chain transfer occurs in hydrocarbon solvents at temperatures² up to 50° .

We have studied the effects of counter-ion and temperature in the anionic polymerisation of styrene in toluene. These studies have provided some evidence for chain-transfer reactions.

In our experiments two initiators were used, (a) dilithiostilbene, which was prepared by refluxing lithium chips and stilbene in tetrahydrofuran under nitrogen for two hr. and (b) disodio- α -methylstyrene tetramer³ which was prepared by the reaction of α -methylstyrene with excess of a dispersion of sodium in tetrahydrofuran under nitrogen at 0° for one hr. Both of these initiator solutions were filtered under nitrogen and standardised with aqueous hydrochloric acid before use.

Toluene and tetrahydrofuran were fractionally

distilled under nitrogen, from sodium and potassium respectively, before use. Styrene and α -methylstyrene were distilled from Lindé molecular sieves type 4A. All polymerisations were carried out in a nitrogen atmosphere. Solutions of the initiators were slowly added to the styrene solutions (in toluene) from a calibrated dispenser with stirring until a faint pink colour of 'living' polystyrene appeared; a pre-calculated amount of the initiator was then added rapidly. After 2 hr. (when polymerisation was complete) the polymers were precipitated in methanol and their intrinsic viscosities were measured in benzene at 25° . Molecular weights were calculated from the equations of Krigbaum and Flory.⁴

The results are shown in the Table; all polymerisations proceeded to 100% conversion of monomer. It can be seen that when lithium is the counter-ion, the polymers always have a molecular weight which is equal to [g. of monomer]/[moles of

TABLE

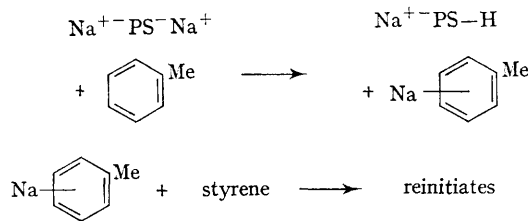
Polymerisation of styrene in toluene

Initiator	Moles of initiator $\times 10^3$	Styrene (g.)	Concentration of styrene (g./l.)	Predicted molecular weight of polymer	Actual molecular weight of polymer	Reaction temperature ($^{\circ}$ C)	Volume of tetrahydrofuran in polymerisation solvent (%)
A	4.40	120	13.0	27,000	30,000	20	0.55
A	23.3	550	60.0	24,000	30,000	45	1.3
A	5.00	500	62.5	100,000	120,000	45	0.52
B	2.58	50	62.5	19,400	19,000	20	1.6
B	2.12	100	100	47,200	16,000	20*	1.1
B	5.0	500.0	62.5	100,000	35,000	20	0.33
B	0.1	10.0	100	100,000	30,000	20	0.50
B	0.1	10.0	50.0	100,000	20,000	20	0.37
B	0.1	10.0	100	100,000	92,000	-78	0.50
B	0.1	10.0	50.0	100,000	90,000	-78	0.37

A = Dilithiostilbene, B = Disodio- α -methylstyrene tetramer, * An exotherm occurred.

initiator]. With sodium counter-ion, however, the pre-calculated molecular weight is not always obtained at room temperatures. It appears that under our conditions, chain transfer in styrene polymerisation may occur at temperatures above -78° if sodium is used as a counter-ion. This transfer process is only apparent if the polymer chains grow to molecular weights $>20,000$ and should therefore be taken into consideration by workers who attempt to use polystyrene 'living ends' in macromolecular syntheses.

The mechanism of this chain-transfer process has yet to be studied, but it might involve the métallation of toluene to produce a sodium compound which is capable of re-initiating the anionic polymerisation of styrene.



When the polymerisation is conducted in pure tetrahydrofuran at 25° no transfer is obtained.¹

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³ C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1962, **66**, 904.

⁴ W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, 1953, **11**, 37.