Experiment 4

Solution Polymerization of Styrene: Determination of the Chain-transfer Constant of Dodecanethiol

Introduction

In this experiment, we will determine the chain transfer constant of dodecanethiol in the solution polymerization of styrene. **IMPORTANT NOTE: DODECANETHIOL STINKS!!! USE ONLY IN A FUME HOOD. A small spill can result in the evacuation of the chemistry building.**

Theory

Without going into an extensive review of the kinetics of radical chain polymerization, let us refresh our memories on the main equations describing these reactions initiated by thermal homolysis of the initiator:

$R_i = 2fK_d[I]$ R_i = rate of initiation, f = initiator efficiency, k_d = initiation rate constant

$R_p = k_p[M][M\bullet]$ R_p = rate of propagation, k_p = propagation rate constant

$R_t = 2k_t[M\bullet]^2$ R_t = rate of termination, k_t = termination rate constant

The kinetic chain length ν is defined as the number of monomer molecules polymerized per radical. If we assume that the reaction has achieved a steady state, then the rate of initiation and the rate of termination are equal, and ν can be given by the ratio of the rate of propagation to the rate of termination:

$$u = \frac{R_p}{R_t} = \frac{k_p\,[M]}{k_t\,[M\bullet]} \tag{1}$$

Substitution of the above equations into equation (1) yields an expression for ν:

$$u = \frac{k_p\,[M]}{2\left(f \times k_d \times k_t \times [I]\right)^{1/2}} \tag{2}$$

From equation (2) we notice that the kinetic chain length is proportional to the monomer concentration and inversely proportional to the square root of the initiator concentration.

Often, the actual kinetic chain length is lower than what would be predicted. This implies the existence of chain transfer reactions, in which the polymer chain is prematurely terminated or the radical is transferred to another species. Chain transfer can occur to monomer, solvent, initiator, adventitious impurities, or to an added chain transfer agent.

$$M_n\bullet \ + \ XA \longrightarrow M_n{-}X \ + \ A\bullet \tag{3}$$

In equation (3), XA may be monomer, solvent, initiator, or any other substance. The rate of chain transfer is given by $R_{tr} = k_{tr}[M\bullet][XA]$. In the general case in which initiation is by thermal homolysis and termination is by coupling, and transfer occurs to monomer, initiator, and chain transfer agent (S),

$$\overline{X}_n = \frac{R_p}{\left(\frac{R_t}{2}\right) + k_{tr,M}[M\bullet][M] + k_{tr,S}[M\bullet][S] + k_{tr,I}[M\bullet][I]} \tag{4}$$

If we define the following chain-transfer constants,

$$C_M = \frac{k_{tr,M}}{k_p} \qquad C_S = \frac{k_{tr,S}}{k_p} \qquad C_I = \frac{k_{tr,I}}{k_p} \tag{5}$$

then equation (4) can be rewritten as:

$$\frac{1}{\overline{X}_n} = \frac{R_i}{2R_p} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]} \tag{6}$$

In the case of chain transfer only to a chain-transfer agent, equation (6) simplifies to:

$$\frac{1}{\overline{X}_n} = \left(\frac{1}{\overline{X}_n}\right)_o + C_S \frac{[S]}{[M]} \qquad (7)$$

where $\left(\frac{1}{\overline{X}_n}\right)_o$ is the sum of the first, second, and fourth terms of equation (6). This expression holds if $[I]^{1/2}/[M]$ is kept constant by appropriate adjustment of the initiator concentration for a series of polymerizations. Thus, a plot of $\frac{1}{\overline{X}_n}$ versus [S]/[M] will yield a straight line of slope C_S.

In this experiment, then, we will perform a number of styrene polymerizations in toluene in the presence of varying amounts of dodecanethiol. We will determine $\overline{X}_n$ using Gel Permeation Chromatography (GPC), and plot $\frac{1}{\overline{X}_n}$ as a function of [S]/[M], and so determine C_S from the slope of the straight line.

NOTE: ALL OF THE FOLLOWING INSTRUCTIONS MUST BE CARRIED OUT IN THE FUMEHOOD.

Experimental Technique

Part I - Solution polymerization of styrene

The recipes for the four reactions that you will perform are given in the table below. These solutions should be prepared **immediately upon commencing the lab**, since these reactions will require three hours, and the subsequent work-up will also take considerable time. Weight out the ingredients into single-neck round bottom flasks (100 mL), put the stopper in place, and secure with elastics. Place the flasks in the 60°C water bath.

Reaction	Styrene (g)	AIBN (g)	Toluene (mL)	Dodecanethiol (g)
(1)	10.0	0.050	70.0	0.010
(2)	10.0	0.050	70.0	0.020
(3)	10.0	0.050	70.0	0.040
(4)	10.0	0.050	70.0	0.080

After 3 hours, remove the flasks from the bath. Then precipitate the polystyrene by adding each polymer solution dropwise from a dropping funnel into separate 1 litre beakers containing 800 mL methanol which are being vigorously stirred. Filter the methanol suspensions through sintered-glass funnels, and wash with three 10 mL portions of methanol. Collect the polystyrene in tared aluminum weighing dishes, and place in an oven (60 ^{o}C) to dry. After drying, determine the weight of polystyrene prepared for each reaction, and calculate the yields.

Part II - Polymer characterization

Prepare four polystyrene solutions containing 4 mg polystyrene per mL of THF. Hand the four samples in to the TA for Gel Permeation Chromatography for molecular weight determination.

Calculations

Plot $\frac{1}{\overline{X}_n}$ against [S]/[M], and determine the slope of the best straight line.

Discussion

Report the chain transfer constant that you obtained, and compare it to the literature value which can be found in the *Polymer Handbook* by Brandrup and Immergut.

Apparatus

100 mL round bottom flasks with stoppers	4
1-L beakers	2
1" stir bars	2
100-mL dropping funnel	2

Chemicals

Styrene, 2,2'-azo-bis-isobutyronitrile, methanol, dodecanethiol, toluene, acetone