Eur. Polym. J. Vol. 27, No. 3, pp. 227–229, 1991
Printed in Great Britain

0014-3057/91 $3.00 + 0.00
Pergamon Press plc

THE MECHANISM OF COPOLYMERIZATION OF STYRENE–MALEIC ANHYDRIDE AS DEDUCED FROM THE BEHAVIOUR OF THE SYSTEM TOWARDS CHAIN-TRANSFERRING TO CARBON TETRACHLORIDE*

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(Received 2 February 1990; received for publication 1 August 1990)

Abstract—Copolymerization of styrene with maleic anhydride was carried out in the following solvent blends: tetrahydrofuran/CCl_4, dioxane/CCl_4 and acetone/CCl_4. Parallel reactions were performed in which CCl_4 was replaced by cyclohexane. The molar ratios of CCl_4 and cyclohexane in the solvent mixtures were varied. The ineffectiveness of CCl_4 as a transfer reagent for this system and the role of the cosolvents as strong electron-donors were studied by following the viscosity average molecular weights ($\bar{M}_v$). An explanation for the behaviour of CCl_4 and the electron-donating solvents is presented with a probable mechanism for the system. A method for the determination of small amounts of halogen in macromolecules is described.

INTRODUCTION

Tsuchida and Tomono [1] found that CCl_4 is an ineffective transfer agent in the alternating copolymerization of styrene (STY) with maleic anhydride (MA). The amount of chlorine determined by the authors as end-groups was nearly 1/50 of that for a typical telomerization. Since CCl_4 is an effective transfer agent for styryl free radicals [2], it seems interesting to investigate further the behaviour of CCl_4 in this system with the intention of obtaining information about the mechanism of copolymerization of STY with MA.

MA is hardly soluble in CCl_4, even at elevated temperatures; hence, we suppose that the copolymerizations carried out by the group mentioned above were not homogeneous. Therefore, we studied the copolymerization in mixed solvents; the effect of CCl_4 was monitored by gradually increasing its molar ratio in the mixture. Chlorine contents of the obtained copolymers and values of $\bar{M}_v$ were determined. Acetone, tetrahydrofuran (THF) and dioxane were chosen as cosolvents with CCl_4 in order to study the effect of nucleophilic solvents on the copolymerization and because these are good solvents for both MA and its copolymers with STY.

Chlorine determinations in these systems are rather difficult, both because its content is extremely small in the copolymers, and because polymers are very difficult to digest for analytical purposes. We developed a method for the determination of Cl suitable for these and similar systems.

EXPERIMENTAL PROCEDURES

All reagents were commercial products and were purified by the usual methods.

Copolymerization procedure

The copolymerizations were performed under reflux at 75° using 0.1% M of benzoyl peroxide as initiator. The concentrations of STY and MA were equimolar and together amounted to a molar concentration of 0.161. The copolymerizations were carried out almost to completion with the solvent mixtures given in Tables 1 and 2.

Determination of molecular weights

Molecular weights of the copolymers were determined by the solution viscosity method using an Ubbelohde Viscometer. THF was used as solvent and molecular weights were calculated using the Mark–Houwink equations [3]:

$$3.98 \times 10^{-4} \bar{M}_v^{0.596}.$$

Structure of copolymers

The ratio of STY to MA was 1:1, within experimental error, in all copolymers. This result has been obtained by the following methods:

1. Potentiometric titration of a known weight of the dried copolymer with CH_3ONa in abs. methanol for the determination of the MA units in the copolymer [4].
2. Elemental analysis of the copolymer using Carlo Erba Elemental Analyser Mod. 1106. With the assumption that MA does not homopolymerize under the conditions of the copolymerization, the copolymers are strictly alternating.

Determination of chlorine content

A 3 g sample of sodium peroxide is mixed with 0.5 g of the copolymer, and then introduced into a 100 ml combustion bomb. An additional 3 g of Na_2O_2 is put over the mixture to assure complete combustion. The bomb is then closed and the mixture is ignited by warming the bottom of the bomb for a short time with a mild flame. Once the combustion starts, it continues to completion without further heating. After cooling, the sodium chloride formed is dissolved in deionized water. The contents of the bomb are then filtered the precipitate thoroughly washed, and the filtrate evaporated to a volume of 100 ml and acidified with HNO_3. A 5 ml sample of the solution is taken and chlorine

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Table 1. Change of $\bar{M}_v$ of copolymers with the variation of molar ratio of CCl_4 in THF, acetone and dioxane

Mole fraction of THF	$\bar{M}_v \times 10^{-3}$	Mole fraction of acetone	$\bar{M}_v \times 10^{-3}$	Mole fraction of dioxane	$\bar{M}_v \times 10^{-3}$
1	10.2	1	53.7	1	29.9
0.8	15.4	0.8	63.5	0.8	38.4
0.6	25.4	0.6	85.0	0.6	120.6
0.4	29.6	0.4	120.6	0.4	141.5
0.2	37.2	0.2	246.0	0.2	167.8

is coprecipitated with $BaSO_4$ as AgCl. A 1 ml sample of 0.2×10^{-2} M $AgNO_3$ is added followed by 1 ml of a solution composed of 2 ml 5×10^{-2} M $BaNO_3$ + 2 ml 5×10^{-2} M Na_2SO_4. The contents are stirred and left for 15 min, and then filtered. The AgCl adhering to $BaSO_4$ is eluted by adding 50% ammonia solution. The resulting solution is evaporated to a volume of 10 ml, and Ag^+ is determined by atomic absorption using Pye Unicam 191 atomic absorption spectrometer.

RESULTS AND DISCUSSION

Table 1 shows the effect of increased concentrations of CCl_4 on $\bar{M}_v$ of the copolymers. Contrary to expectation, $\bar{M}_v$ increases with increasing concentration of CCl_4. The relationship is not linear in the case of acetone and dioxane as cosolvents and shows discontinuity, suggesting that there are at least two factors influencing the variation of $\bar{M}_v$ with the concentration of CCl_4. One of the factors is definitely the decrease of solubility of the copolymers with increase in CCl_4 concentration. Under these conditions, an increase in reaction rate and molecular weight can be expected [5].

This consideration does not explain, however, the ineffectiveness of chain transfer of styryl radicals to CCl_4 in the present copolymerization; according to Mayo [2] only oligomers should be obtained at increased CCl_4 concentrations. In fact, Kharash *et al.* [6] observed that, at high concentrations of CCl_4, the degree of polymerization for most vinyl monomers is unity.

Two alternative explanations could be considered for this observations:

(a) Acetone, THF and dioxane are strong electron-donors which compete with STY for complexation with MA. If the STY–MA complex were very reactive as assumed by some authors [7], then the effect of increased CCl_4 concentration is definitely due to the accompanying increase in the concentration of STY–MA complex. It is well known that the concentration of this complex increases in non-polar solvents [8]. Furthermore, the complex should add to the growing free radical at the STY end,so that only MA radicals are found at the ends of the growing chains:

$$\mathrm{SMA}^{\cdot} + \mathrm{SMA} \rightarrow \mathrm{SMASMA}^{\cdot}.$$

(b) Nucleophilic free radicals show great reactivity towards reagents that are electron-acceptors and vice versa. Rätzsch and Steinert [9] found that MA (a strong acceptor) is 850 times more reactive than STY (a strong electron-donor) towards the cyclohexyl radical (a donor-type radical). In this case, we expect that the styryl radical should react much more quickly with MA than with CCl_4; a reaction between MA radical and CCl_4 is expected to be extremely slow because both are electrophilic. This explanation is in line with two critical reviews [10, 11] which have shown that there is no compelling evidence in favour of the complex participation. All arguments presented in the literature to support the complex model could also be explained in terms of the crosspropagation model. One of these arguments is the observed decrease in the rate of copolymerization in solvents capable of strongly complexing with MA, and hence decreasing the concentration of STY–MA complex. Another explanation for this observation is that the electrophilicity of a reagent (MA) is partially compensated in the case of complexation with a nucleophilic solvent; therefore, electron-donating solvents complex with MA and reduce its electrophilicity and in consequence its readiness to react with the styryl radical. Likewise, MA radicals associated with nucleophilic solvents would show a decreased reactivity towards STY.

Proceeding with this reasoning, complex formation between monomers would lead to a decrease in their reactivities because of partial compensation of their donor-acceptor properties.

Table 2. Change of $\bar{M}_v$ of copolymers with variation of molar ratio of cyclohexane in THF, acetone and dioxane

Mole fraction of THF	$\bar{M}_v \times 10^{-3}$	Mole fraction of acetone	$\bar{M}_v \times 10^{-3}$	Mole fraction of dioxane	$\bar{M}_v \times 10^{-3}$
1	10.2	1	53.7	1	29.9
0.8	15.4	0.8	93.4	0.8	102.1
0.6	17.6	0.6	127.8	0.6	153.1
0.4	17.8	0.4	197.3	0.4	177.4
0.2	16.1	0.2	246.0	0.2	163.7

We adopted a method that combines combustion of the copolymers on a macro-scale, and then applying a micro-procedure for the determination of chlorine. Table 3 gives the number of chlorine atoms per copolymer molecule in three solvent blends.

Table 3. Results of quantitative analysis for chlorine in copolymers of STY with MA

Copolymerization medium	Number of runs	No. of Cl-atoms per molecule of copolymer
CCl_4–acetone	12	3.1 ± 0.1
CCl_4–THF	12	0.87 ± 0.03
CCl_4–dioxane	12	2.3 ± 0.08

Mole fractions of CCl_4 in the copolymerization mixtures were 0.8.

Under usual copolymerization conditions, the concentration of the complex is considerable. Collision of the complex with the growing chain ends is inevitable and participation of the complex in the copolymerization is very probable. According to the reasoning presented above, a cross collision of the complex with the free radicals at chain ends has more chance of success than a collision from the side of the same monomer, and the chance of cross collision of a free monmer is greater than the chance of its cross collision within the complex.

We have performed parallel copolymerizations in which CCl_4 was replaced by cyclohexane. The results are shown in Table 2. The values of $\bar{M}_v$ are in some cases higher in this solvent, meaning that CCl_4 acts as a chain transfer reagent but its reactivity as such is very small compared with that in usual telomerizations.

Chlorine content of the copolymers

In order to overcome the difficulties in estimating chlorine in polymers arising from its extremely small concentration and the difficulty in combusting the copolymers.

Telomerization of a monomer can be represented thus:

$$\text{Initiator} \rightarrow 2R^{\cdot}$$

$$R^{\cdot} + CCl_4 \rightarrow RCl + CL_3C^{\cdot}$$

$$Cl_3C^{\cdot} + M \rightarrow Cl_3C\,M^{\cdot}$$

$$Cl_3C\,M + Mn \rightarrow Cl_3C(M)\,nM^{\cdot}$$

$$Cl_3C(M)nM + CCl_4 \rightarrow Cl_3C(M)nMCl + Cl_3C^{\cdot}.$$

This scheme predicts four chlorine atoms per molecule. The copolymers contained three chlorine atoms in CCl_4–acetone as a solvent meaning that the chains are not terminated by chlorine. In THF–CCl_4, only 0.87 chlorine atoms per molecule are found. In the presence of THF, the lowest values of $\bar{M}_v$ were obtained because THF itself acts as a transfer reagent. Jacobs and Ecke [12] found that free radicals initiate a reaction between THF and MA to form (tetrahydro-2-furyl)-succinic anhydride.

Our results contradict those obtained by other authors [1]. We think that the low solubility of MA in CCl_4 accounts for the very low chlorine contents obtained previously.

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