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Motoo Horiba[a]; Natsuki Yamashita[a]; Toshihisa Maeshima[a]
[a] Department of Applied Chemistry, Faculty of Science and Engineering Kinki University Kowakae, Higashi-Osaka, Japan

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Additive Effect of p-Substituted Phenols on the Anionic Polymerization of Acrolein Induced by Imidazole

MOTOO HORIBA, NATSUKI YAMASHITA, and
TOSHIHISA MAESHIMA

Department of Applied Chemistry
Faculty of Science and Engineering
Kinki University
Kowakae, Higashi-Osaka, 577 Japan

ABSTRACT

Anionic polymerization of acrolein (AL) by imidazole in the presence of several p-substituted phenols such as phenol, p-methylphenol, and p-nitrophenol were kinetically carried out in tetrahydrofuran at 0°C. The initial polymerization rate R_p was estimated from the rate of monomer consumption by means of gas chromatography. A linear correlation was obtained from Hammett's equation, $\log R_pX/R_pH = 0.22$. Meanwhile, the polymerizabilities were found to be in the following order: p-methylphenol > phenol > p-nitrophenol. The additive effect of phenols was kinetically discussed on the basis of these results.

INTRODUCTION

Anionic polymerization of acrolein (AL) in the presence of imidazole (Im) catalyst has been studied in tetrahydrofuran (THF) or methanol below room temperature [1]. Several other polar vinyl monomers

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such as methyl vinyl ketone, acrylamide, and methyl methacrylate also polymerize similarly by this initiation system [2]. The overall rate of polymerization R_p for AL was expressed by the equation $R_p = k[Im][AL]^2$ (in THF at 0°C). The kinetic investigations revealed that the polymerization is initiated by a thermodynamic equilibrium between the imidazole and 3-(N-imidazolyl)propanal as an initial adduct in the initial polymerization step. Interestingly, the overall R_p and the number-average molecular weight $\overline{M}_n$ of the polymer in the presence of water [1], dimethylsulfoxide [1], and several amide compounds [3-5] were increased respectively by the interaction between the aldehyde group and these additive. In addition, the anionic polymerization of AL in the presence of polyacrylamide indicated matrix polymerizability [3-6]. The presence of polyacrylamide increased the rate of initial polymerization. While the $\overline{M}_n$ of polyacrolein decreased with increasing polyacrylamide, the content of free aldehyde group as a sidechain in polyacrolein increased markedly. These interesting results suggest interaction between monomer and additive. At the present stage, however, there are many points which are uncertain.

This investigation was performed to clarify thses points by the use of several p-substituted phenols as additives.

EXPERIMENTAL

Materials

Acrolein (AL) was prepared in the manner described previously [1]. Imidazole (Im) was purified by recrystallization from benzene. Purification of phenol and p-substituted phenols such as p-methyl- and p-nitrophenol were carried out in the usual way.

Polymerization Methods

All operations were carried out in a vacuum line under nitrogen. The required amounts of Im and THF were placed in a tube. Then a fixed amount of AL and the additive were added to start the polymerization reaction. The polymerization was stopped in a large amount of ether containing hydrogen chloride, and the precipitate was filtered to dryness.

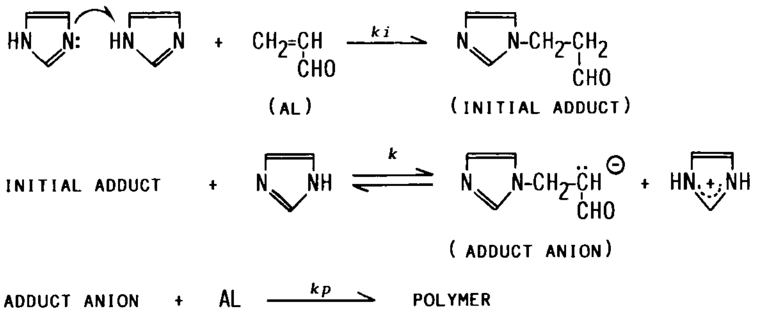
Kinetics

The initial polymerization rate R_p was estimated from the decreasing concentration monomer by gas chromatography. A straight-line relationship between the reaction time and the consumption of monomer was observed in the initial reaction.

RESULT AND DISCUSSION

Polymerization Results

In a previous paper [1] we revealed the polymerization mechanism of this anionic polymerization system. The polymerization mechanism was indicated as the following scheme:



Anionic polymerizations of AL in the presence of p-substituted phenols were carried out in THF at 0°C. Figure 1 shows that the time-conversion curves vary depending on the type of phenol derivative, and that the presence of phenols increased the rate of polymerization. The number-average molecular weight of polymers increased with increasing polymerization time.

The kinetic data are shown in Table 1. The presence of phenols increases R_p, which decreases as the polymerization proceeds.

Additive Effect of p-Substituted Phenols

From these results a linear correlation was obtained by Hammett's equation $\log R_pX/R_pH = 0.22$ (Fig. 2). Evidently the reaction is governed by the increasing polarity of the hydroxyl group of the phenoxide anion $C_6H_5O^-$. In addition, it may be considered that the reactivity of the phenoxide anion was increased because of lack of solvation between the phenoxide anion and THF. On the other hand, in the initial step the polymerizabilities were found to be in the following order: p-nitrophenol > phenol > p-methylphenol. By considering all these results, the additive effect of phenols may be assumed as shown in Fig. 3. In the case of interaction between phenol and the carbonyl group of electron-

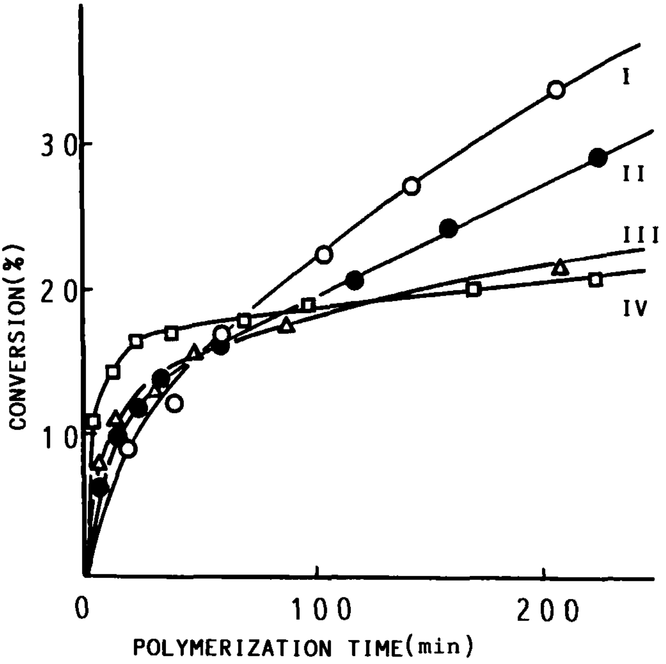


FIG. 1. Time-conversion curves in tetrahydrofuran at 0°C. Polymerization conditions: [AL] = 2.31 mol/L, [Im] = 0.3 mol/L, [p-substituted phenol] = 0.05 mol/L. I: No addition. II: p-Methylphenol. III: Phenol. IV: p-Nitrophenol.

accepting monomer (Fig. 3a), the δ^+ of β-carbon is increased by an increased charge density on the vinyl group. Therefore, imidazole, as a nucleophilic reagent, is liable to attack the β-carbon.

On the other hand, in the subsequent propagation polymerization step (Fig. 1), the polymerizabilities resulted in the following order: p-methylphenol > phenol > p-nitrophenol. Generally, when a carbonyl compound is mixed with an alcohol, the alcohol molecule adds to the carbonyl double bond to form a hemiacetal or a hemiketal up to the equilibrium state [7]. The reactivities of AL with the hydroxyl group and phenol have been explained by Morris [8] and Schulz [9, 10]. On the other hand, the interaction of poly(vinylpyrrolidone) with various p-substituted phenols was reported by Inoue et al. [11]. This result strongly suggests that the interaction between the carbonyl group of poly(vinylpyrrolidone) and phenols is due to an electrostatic interaction or hydrogen bonding. In our work the interaction (Fig. 3b) between the end group of the polymer chain and p-substituted phenols may be considered in terms of the above reasons. In this case it may

TABLE 1. Kinetic Results of Polymerization of AL$_a$ Induced by Imidazole in the Presence of p-Substituted Phenols[a]

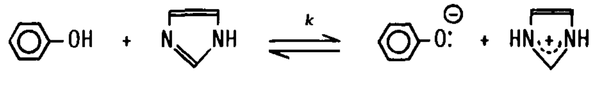
Phenol	Concentration of phenol, mol/L	$R_p \times 10^2$, mol/(L·min)	R_p/R_{p0}
No addition	0	3.08	1
Phenol	0.05	5.83	1.9
	0.15	7.54	2.5
p-Methylphenol	0.05	5.27	1.7
	0.15	6.15	2.0
p-Nitrophenol	0.05	8.60	2.8
	0.15	9.23	3.0

[a] Polymerization conditions: [AL] = 2.31 mol/L, [Im] = 0.3 mol/L, in THF at 0°C under N_2. GLC conditions; Celite 545 (60-80 mesh) containing methoxyPEG, He as carrier gas.

be that the polymerizability was increased by the electron-donating group of p-substituted phenols.

Structure of the Polymer

In a previous paper [1] we reported on the structure of the polymer. However, phenols were added to the polymerization system in this study, and it is necessary to consider an equilibrium between Im and phenol according to



Acrolein, as an electron-accepting monomer, may be polymerized by the phenoxide anion. The structure of the polymer obtained was investigated by IR spectroscopy. The IR spectra (Fig. 4) of these polymers revealed absorption bands of Im (3 200, 1 600-1 500, and 1 400-1 200 cm^{-1}) and the characteristic absorption bands of poly-AL (1 700-1 680 and 1 140-900 cm^{-1}). However, it was found that no absorption band of phenyl ether (1 220 cm^{-1}) can be recognized clearly. Accordingly, it was concluded that AL is not polymerized by the phenoxide anion.

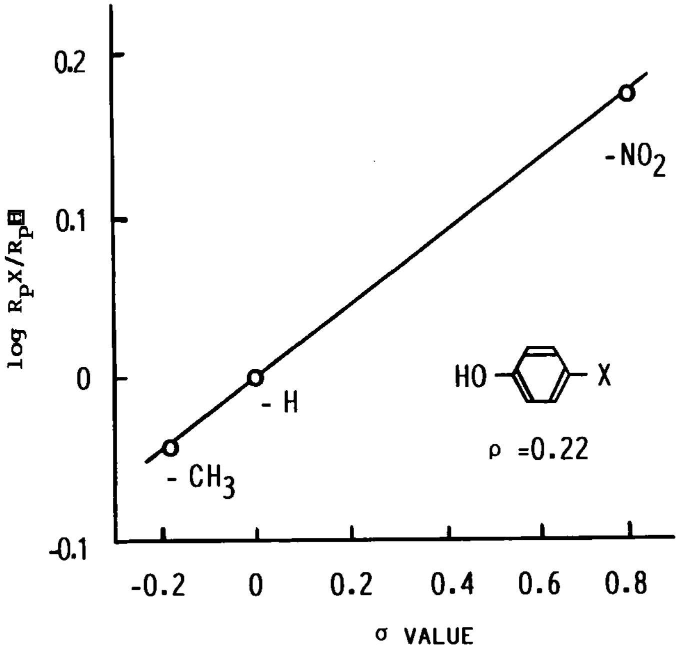


FIG. 2. Relation between log R_pX/R_pH and Hammett's σ-value.

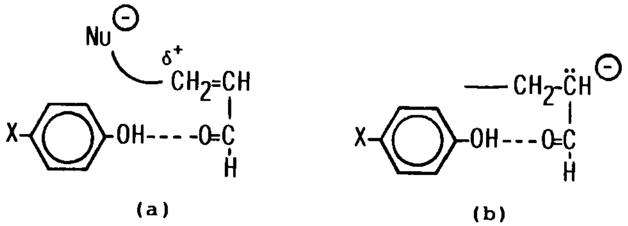


FIG. 3. Interactions between p-substituted phenols and carbonyl groups in monomer or polymer.

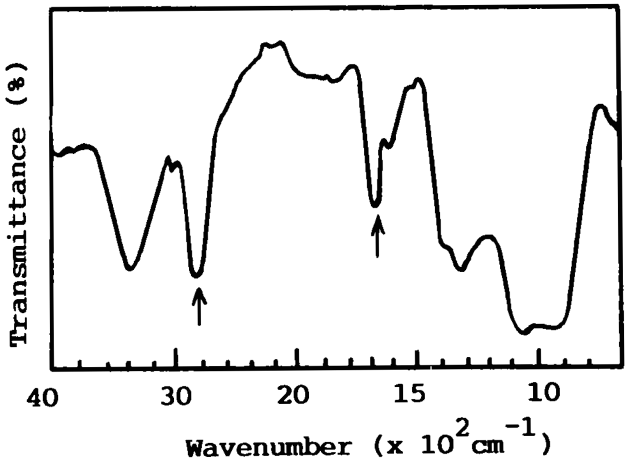


FIG. 4. IR spectrum of poly-AL (KBr disk).

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