Optimized Synthesis of Styrenic Tackifying Resins

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ABSTRACT: Technical pure styrene monomer was cationically polymerized either alone or with α-metylstyrene to prepare tackifying resins. Anhydrous aluminum chloride dispersed in toluene was used as the catalyst. The polymerization was optimized with emphasis on practical viewpoints, and incremental monomer addition method was used in all the syntheses. Certain parameters affected on the reaction and on the resin characteristics, i.e., starting reaction temperature, catalyst percent, monomer and comonomer concentration, and solvent type were investigated. Post-heating of the resins was briefly studied as well. Number average molecular weight (M_n) and poly-dispersity (PDI) of the resins were determined by size-exclusion chromatography. Changes of M_n and PDI, as well as the reaction rate and yield versus variation of the mentioned parameters, were basically investigated according to the mechanism of carbocationic polymerization. Finally, the structure of the synthesized resins was confirmed by IR and NMR spectroscopy. A graphical method was proposed to quantify comonomer composition of the copolymeric resins by using of the ratio of aromatic to aliphatic protons peak area from the corresponding NMR spectra. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2109–2119, 2001

Key words: tackifying resin; styrene; α-methylstyrene; cationic polymerization; aluminum chloride; average molecular weight; polydispersity

INTRODUCTION

Synthetic adhesives are mostly formulated from a backbone polymer (the base row material), a tackifying resin, and a carrier to give the necessary consistency for a given application, which may be solvent, water, or heat. Therefore, synthetic adhesives may be classified according to the carrier as: (a) solvent-borne or contact adhesives, (b) water-borne or dispersed adhesives, and (c) hot-melts. In addition to adhesives, tackifiers are used in other numerous applications, e.g., surface coatings, sealants, printing inks, and additives in rubbers.

Tackifying resins are added to the backbone polymers to improve the stickiness, specific adhe-

sion, and wetting; in short, they are added to regulate rheological properties of the final adhesives or other systems. To function properly, a good tackifier must exhibit three fundamental properties: (i) it must be reasonably compatible with the base polymer, (ii) it must have a very low molecular weight (MW) relative to the base polymer, and (iii) it must have a glass transition temperature (T_g) that is higher than that of the base polymer.[1]

The tackifying resins can be categorized as terpene resins, rosin resins, and hydrocarbon resins. The latter may be subclassified into petroleum-based, coal tar-based (coumaron-indene), and pure-monomer-based resins. Petroleum resins, which have been recently critically reviewed,[2] may be distinguished as three main classes: aliphatic(C5), aromatic(C9), and dicyclopentadiene (DCPD) resins. Unlike the rosins, the hydrocarbon resins are true polymers derived from petro-

leum or coal. Thus, the type of the monomers and the polymerization processes determine the performance characteristics (compatibility, MW, and T_g) of each resin, in turn, define the ability of a resin to act as a tackifier.

Tackifying resins from technical pure monomers are produced from commercially available high-purity aromatic monomers, such as styrene and its alkylated homologs.[3] These rapidly developing resins are very stable and light-colored to water-white. Examples of these products are Piccolastic of Hercules, Inc. (based on styrene) and Amoco Resin 18 (based on α-methylstyrene).[4]

Preparation methods for the pure-monomer-based resins are basically the same as for the C9 resins, by treating particular feeds with $AlCl_3$, less frequently with BF_3, or other Friedel-Crafts acids, sometimes in the presence of various promoters such as HCl and t-BuCl, at various temperatures (from -20 to $+100°C$) depending on the available feedstock and desired end product.[2–4] Quenching of the cationic polymerizations by various bases, such as water, alkalis, lime, ammonia, and removing of the volatiles by distillation, are typical final purification operations mentioned in the literature.[2–7]

A literature survey[2] based on the Chemical Abstracts revealed that all the reports on synthesis of the resins are as patents, except a few scattered papers.[8–10] Class and Chu,[11–13] in a series of investigation on the viscoelastic properties of rubber-resin blends, have studied the effects of the chemical structure, MW, and concentration of the tackifying resins including polystyrene, poly(vinylcyclohexane), and poly-(*tert*-butylstyrene). They have not presented any details about the resins preparation, although the mentioned resins are said to be synthesized by themselves.

The present study is concerned with optimization of synthesis and properties of some styrene-based tackifying resins through investigation of certain parameters controlling the resin characteristics.

EXPERIMENTAL

Materials and Instruments

Styrene and all solvents were technical grade and used without purification. α-methylstyrene (αMeSt) and anhydrous aluminum chloride was obtained from Merck and used as received. Size-exclusion chromatographic analysis of resins (in tetrahydrofuran [THF] as solvent) was performed at 30°C with a Waters 150C GPC system equipped with Ultrastyragel columns (10^4, 10^5, 10^6 Å), a data processing system, a RI detector, and a calibration curve for polystyrene standards. IR spectra were measured by a Philips PU 9712 infrared spectrophotometer. Sixty Megahertz CW ^{1}H-NMR spectra were obtained on a JEOL JMX60SI spectrometer using tetramethylsilane as an internal standard (solvent CCl_4).

Synthesis

Several procedures—including preparation and use of toluene/(HCl)/$AlCl_3$ catalyst in a few manners; use of a very dilute solution of $AlCl_3$ in toluene or chloroform, instead of dispersion form; changing the sequence of monomer-catalyst addition to the reactor; use of dilute aqueous HCl, NH_4OH, or water for quenching the reaction mixture; and using the vacuum distillation, solvent evaporation, and steam distillation followed by drying of the product—were carried out to lead to the best way to control the reaction and to achieve more applicability and repeatability. An optimized general procedure consisting of rapid addition of monomer(s) solution to the catalyst dispersion (incremental monomer addition) was applied.

A 250-mL, four-necked kettle equipped with a reflux condenser, mechanical stirrer, dropping funnel, and thermometer was charged with given amounts of toluene and powdered anhydrous $AlCl_3$. A solution of styrene in toluene was added to the vigorously stirred catalyst dispersion, in a rate of 4–5 mL/s, at a given starting temperature. The adding solution and the overall monomer(s) concentration were 1:1 v/v and 34 wt %, respectively, unless in the case of the experiments studying the effect of monomer concentration.

An intensive exothermic reaction was occurred during a few seconds, the temperature rapidly increased, and the mixture color changed into orange and then dark red. The stirring was continued for an additional fifteen minutes to complete the reaction. The mixture was then poured into a beaker and gently stirred magnetically after adding about 1 mL of water. Complete decomposition of the catalyst was detected by discoloring of the mixture. It was allowed to stand overnight to settle down the sediments. The semiclear supernatant was then decanted and rota-evaporated to remove the solvent. Finally, the concen-

trated resin solution was poured into a dish to heat in an air-recirculating oven at 70°C for 5 h. Trace amounts of solvent was eliminated in a vacuum oven (25 torr, 70°C, 5 h). A clear solid to viscose liquid resin was yielded. The resins were soluble in acetone, MEK, THF, CCl_4, $CHCl_3$, benzene, and chlorobezene. They were partially soluble in hexane and heptane, but insoluble in aliphatic alcohols.

This general procedure should be appropriately modified when water-solvent density difference was great. Thus, in n-heptane (batch no. 86) the pasty settled product was separated from the heptane phase, transferred to a beaker by dissolving in 3 × 10 mL of toluene, and treated with water. In the case of CH_2Cl_2 solvent (batch no. 97), after the reaction completion, 15 mL of toluene and then 10 mL of $15M$ H_2SO_4 were gradually added to discolor the mixture. The next operations were the same as discussed above.

Certain parameters affecting on the resin characteristics, i.e., reaction temperature, catalyst amount, monomer and comonomer concentration, as well as solvent type and post-heating were investigated.

RESULTS AND DISCUSSION

Varieties of pathways were examined to achieve a versatile synthetic and work-up procedure comprise the shortest time, the simplest equipment, the highest yield, and the highest product quality. Thus, the best batchwise procedure was resulted as presented in the experimental section.

Catalyst

Anhydrous $AlCl_3$ is known as the most effective and commonly used catalyst (initiator) among the Lewis acids. However, its solubility is low in nonpolar organic solvents, making quantitative studies difficult.[14] In addition, it is moisture sensitive. So, with an emphasis on simplicity and brevity of the resin preparation in a practical viewpoint, it was consumed without further purification in a form of dispersion.

Two series of experiment was performed to determine the optimum amount of the catalyst with the monomer wt % of 34 at both initial reaction temperature of 0°C and 25°C (Table I). According to the data, high amount of $AlCl_3$ was resulted in higher reaction temperature increase (ΔT), which

Table I   Reaction Temperature Increase (ΔT), Yield, and Number Average Molecular Weight (M_n) and Distribution (PDI) vs Catalyst Weight Percent[a]

| Batch No.	$AlCl_3$ wt %	ΔT (°C)	Yield (%)	M_n	PDI
(A) Starting Temperature = 0°C					
36	0.05	8	13	1470	2.54
38	0.10	11	16	1610	2.49
39	0.15	14	64	1538	2.57
41	0.30	36	~100	1504	2.25
42	0.40	57	~100	1344	2.41
44	0.70	85	~100	1256	2.47
45	1.00	87	~100	1293	2.31
(B) Starting Temperature = 25°C					
89	0.05	31	19	1476	1.13
90	0.10	38	28	1522	1.74
91	0.20	49	73	1293	1.29
92	0.30	67	~100	1480	1.52
93	0.40	82	~100	1335	1.73
94	0.70	86	~100	1231	1.92
95	1.00	87	~100	1129	1.67

[a] The appearance of the obtained resins: Nos. 36–39, white solids; Nos. 41 and 42, white semisolids; the others, yellow semi–solids.

means higher rate of polymerization (R_p) in agreement with the following equation[15]:

$$R_p = -\frac{d[M]}{dt} = \frac{k_i k_p K}{k_{tr}} \frac{[AH][C][M]^2}{[S]} \quad (1)$$

where $[C]$, $[AH]$, and $[M]$ stand for catalyst, cocatalyst (coinitiator), and monomer concentration, and k_i, k_p, and k_{tr} are rate constants of initiation, propagation, and transfer, respectively. K is the equilibrium constant of the reversible catalyst-cocatalyst reaction. $[S]$ stands for concentration of any compound responsible for the transfer reaction (e.g., monomer, solvent, nucleophile, impurity).

As pointed out in the literature,[4,14] aluminum chloride alone does not initiate polymerization of styrene in dry media. In the present work, neither monomer nor solvent(s) was dried and the reaction was not protected from moisture. Thus, the cocatalyst required, i.e., trace H_2O, was automat-
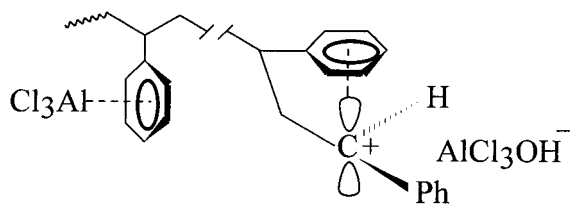
Scheme 1

ically guaranteed. In such a binary system, $AlCl_3$ initiates the polymerization of styrene via a catalyst-cocatalyst complex (eq. 2) rather than self-ionization ($2AlCl_3 = AlCl_2^+ \ AlCl_4^-$).

$$AlCl_3 + HOH \text{ (trace)} \underset{}{\overset{K}{\rightleftharpoons}} H^+, AlCl_3OH^-$$
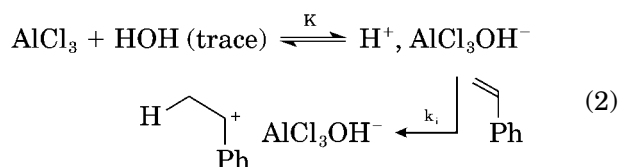
Meanwhile, the dark red color of the polymerization mixture is due to the formation of donor-acceptor (charge transfer) complexes between the aromatic rings and the carbenium ions as well as $AlCl_3$ (Scheme 1). As soon as these complexes decompose by quenching the reaction, the mixture discolors.

No important variation was observed in M_n and PDI, which may be attributed to constant $[M]/[S]$ ratio that should lead to a constant number average degree of polymerization[15] ($P_n = M_n/104$):

$$P_n = \frac{k_p[M]}{k_{tr}[S]} \tag{3}$$

The only obvious difference between A and B data series summarized in Table I is concerned with PDI and, in a lesser extent, with M_n values. Broader MW distribution (higher PDI) obtained at 0°C, due to slower initiation and slower exchange between active sites at lower temperatures.[14] Moreover, probability for any kind of transfer increases with increasing the reaction temperature. As a result, k_{tr} increasing leads to M_n decreasing, according to the eq. (3). (Compare the M_n values corresponding to $AlCl_3$ wt % of 0.10, 0.30, 0.40, 0.70, and 1.00 in A and B series of data.)

Reaction yields were determined to be quantitative for 0.30 wt % of $AlCl_3$ and more. According to data from A and B experiment series presented

in Table I, 0.40 wt % of the catalyst was chosen as an optimized concentration to ensure achieving quantitative yield. Higher concentrations were caused some problems due to sudden intense reaction temperature increase, and sedimentation incompleteness in the purification period as well.

Temperature

Temperature, as a valuable parameter to MW control, was investigated by passing the batch polymerization mixtures through a temperature range, from the initial starting temperature (T_s) of 25–70°C up to final (maximum) temperature (T_{max}) of 108–112°C, i.e., around the boiling point (bp) of the solvent, toluene. In fact, heat of the polymerization is the source of the temperature increase. The results are tabulated in Table II. Lower starting temperatures (batch nos. 48–52) gave lighter-colored resins, whereas higher starting temperatures, specially 60, 65, and 70°C, resulted in resins having darker colors.

Regarding the molecular weights, higher polymers are expected to form at lower temperatures,[15] but the measured M_n values do not follow such clear changes. To explain possible reasons for the deviation, it has to be notified the chemistry of transfer reactions which are the most important chain-breaking reaction in cationic polymerization of alkenes. As demonstrated in Scheme 2, the major transfer reactions in cationic polymerizations are β-proton elimination to form unsaturated end groups and Friedel-Crafts alky-

Table II Effect of the Reaction Starting Temperature (T_s) on the Resin Characteristics[a]

Batch No.	T_s (°C)	T_{max} (°C)	M_n	PDI	Appearance[b]/ Gardner Color
48	25	107	1387	1.67	SS/1
49	30	110	1215	1.82	SS/1
50	35	112	948	2.03	VL/2
51	40	111	1319	1.46	VL/2
52	45	110	988	1.97	VL/2
53	50	111	1217	1.72	SS/2
54	55	109	1379	1.55	SS/4
55	60	111	1146	1.72	SS/6
56	65	110	1135	1.80	SS/6
57	70	110	1177	1.76	SS/7

[a] All the polymerizations were carried out using 0.4 wt % of $AlCl_3$ and lead to quantitative yields.
[b] SS = semi solid; VL = high viscose liquid.

Scheme 2
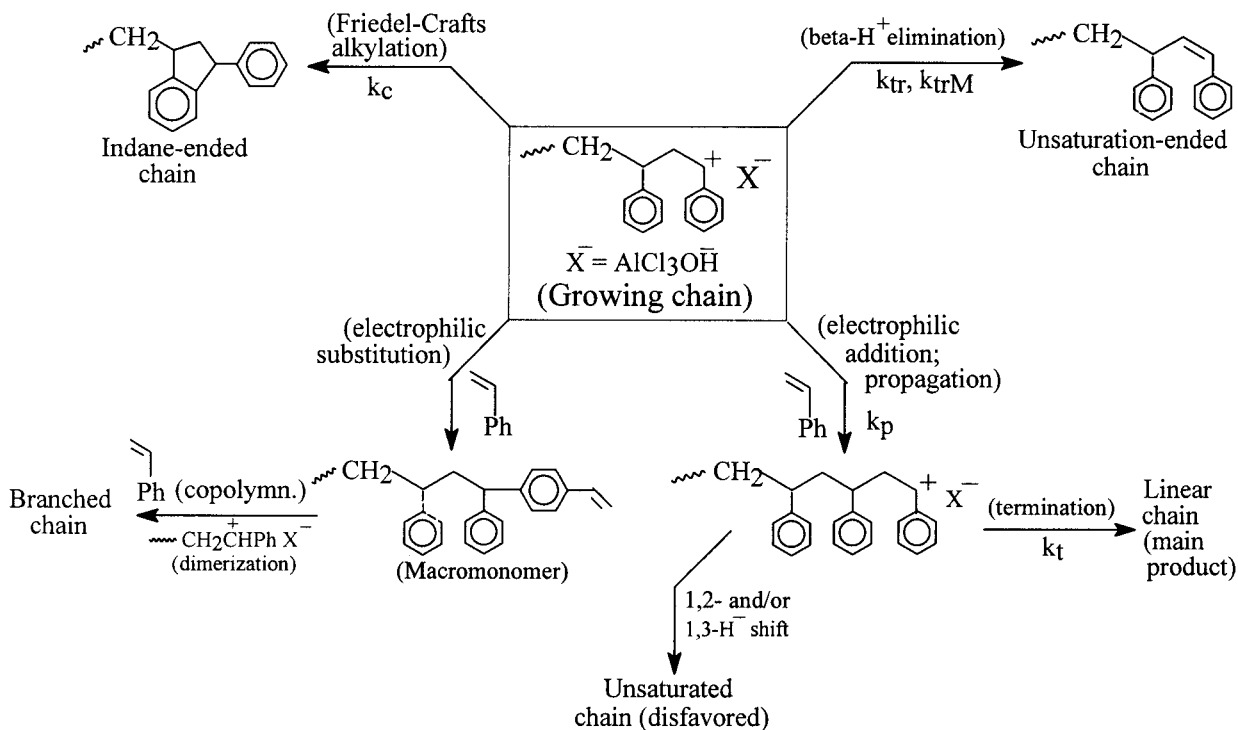
lation of aromatic rings; both generate protons capable of re-initiation. Transfer may also be a prerequisite to termination, which occurs subsequent to transfer.

Temperature affects all the elementary reactions. Since the β-proton elimination has a higher activation energy than electrophilic addition (initiation and propagation), then transfer is reduced $(k_{tr}, k_{trM} < k_p)$ and higher molecular weight polymers are generally formed at lower temperatures. On the other hand, Friedel-Crafts alkylation (e.g., indane formation) has lower activation energy than propagation $(k_c > k_p)$, and at low temperatures it may become the dominating transfer reaction. In such a case, decrease of temperature should initially increase M_n but then may reduce it when intra-molecular Friedel-Crafts cyclization will become faster than elimination.[16]

Furthermore, although transfer generally decreases the average MW obtained from a polymerization, it can also lead to an abrupt increase in MW at high conversion.[17,18] In view of the fact that quantitative yields were obtained in the present experiments, the MW of the resins can increase at high monomer conversion by both intermolecular Friedel-Crafts alkylation and by macromonomer formation followed by copolymerization and dimerization (Scheme 2).

Monomer Concentration

Effect of the monomer concentration, in a constant catalyst to monomer weight ratio of 0.02, was investigated. The results are given in Table III. It can be obviously concluded from the table that ΔT, as a measure of the reaction rate, increases with the monomer concentration increase, which is in agreement with eq. (1). This fact is properly shown in Figure 1 through comparing the temperature-time profile correspond-

Table III Effect of the Monomer Concentration on the Polymerization and Resin Characteristics

Batch No.	Monomer wt %	ΔT^{a} (°C)	Yield (%)	M_n	PDI
66	10	17	73	1378	1.61
67	20	58	90	1702	1.58
69	30	81	96	1638	1.65
58	34	83	100	1356	1.70
70	40	85	99	1418	1.72
71	50	86	99	1187	2.65
72	60	88	98	1460	1.79

^{a} Reaction temperature increase, from 25°C to the maximum reaction temperature.
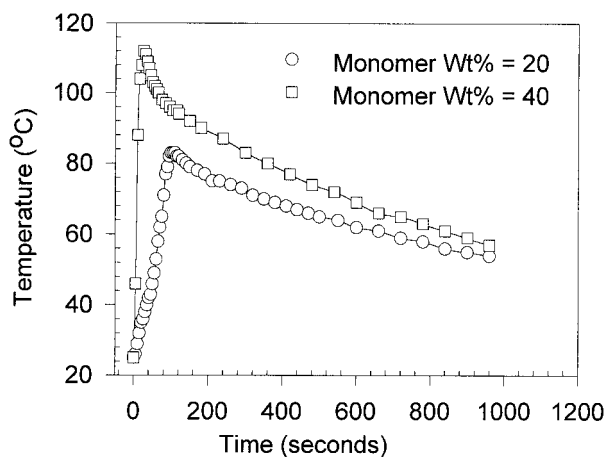
Figure 1   Temperature variation versus reaction time (starting from the time of addition of the monomer solution) corresponding to the monomer wt % of 20 and 40, leading to the yield of 90 and 99%, respectively.

ing to monomer wt % of 40 and 20. According to the eq. (3), an increase in the monomer concentration should provide higher MW. But the M_n variations given in Table III do not meet the expectancy.

Among the several reasons for the deviation from ideal behavior,[14] slow and incomplete initiation, as well as the change of average dielectric constant of the reaction media, seems to be more important. The reaction medium polarity (estimated from its dielectric constant) influence the ionization equilibria and the rates of exchange of growing species. The medium may also interact in a specific way with the intermediates by the formation of onium ions, such as oxonium, which are cationic species with expanded valencies formed by reaction of carbenium ions with noncharged nucleophiles, e.g., H_2O [see eq. (4)].
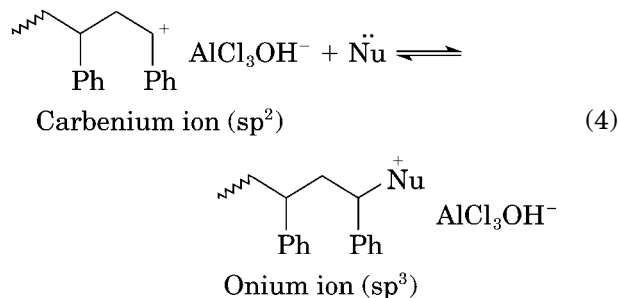
Ion pairs are less dissociated in a medium having low dielectric constant. However, initiation may also be slower and incomplete. On the other hand, the rate of the unimolecular transfer, a reaction

between an anion and a β-proton of the growing end (ion-ion interaction), eq. (5), is accelerated in less polar medium in comparison with propagation, which is an ion-dipole reaction [see eq. (6)].
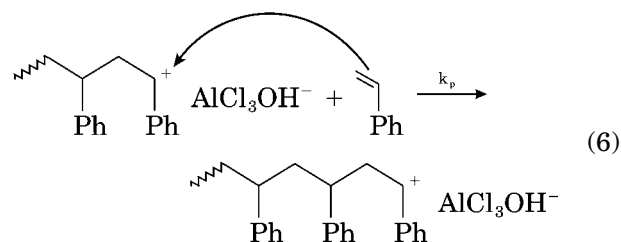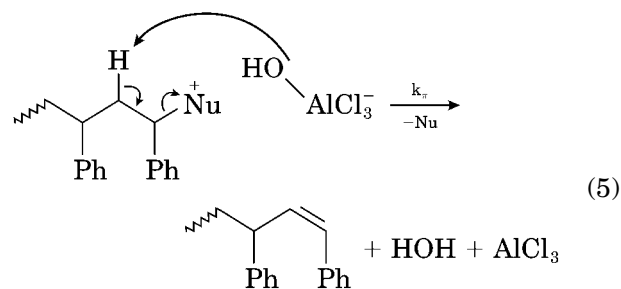
Thus, in lower monomer concentration (medium having slightly lower dielectric constant), lower PDI due to faster exchange may be expected, but, at the same time, lower M_n and higher PDI due to stronger transfer can also be expected.

Finally, according to the results given in Table III, the reaction yields were increased by higher monomer concentrations. The monomer wt % of about 35% was recognized to be the optimum amount lead to the highest (quantitative) yield.

Comonomer Effects

Styrene monomer was cationically copolymerized with αMeSt as a comonomer at an optimized reaction conditions: $AlCl_3$ wt % of 0.4, monomer(s) wt % of 34, starting temperature of 25°C (see experimental section). The color of the αMeSt-contained resins was basically similar to that of the homopolymeric styrene resins. However, the viscosities of the copolymeric resins were somewhat lower than that of the wholly styrenic resins; they was gradually dropped when the comonomer constituent increased. Some empirical results versus different weight percent of the comonomer are given in Table IV.

According to Table IV, the maximum reaction temperature (T_{max}) was decreased with increasing of the comonomer wt %, and at the same time,

Table IV Effects of Comonomer (αMeSt) Weight Percent on the Polymerization[a] and Resin Characteristics

Batch No.	Comonomer wt %	ΔT[b] (°C)	$t \to T_{max}$[c] (s)	Yield (%)	M_n	PDI
48	0.0	82	22	~100	1387	1.67
60	13.3	79	95	~100	2244	4.10
61	26.7	76	105	~100	1213	1.77
62	40.0	73	150	~100	1103	1.89
63	53.3	62	200	98	1228	1.93
64	66.7	45	230	96	1457	1.42
65	80.0	38	275	85	1248	1.48
59	100.0	27	350	61	931	1.78

[a] Amount of the common reactants: $AlCl_3$ = 0.4 wt %, total monomers = 34 wt %.
[b] Reaction temperature increase, from 25°C to the maximum reaction temperature (T_{max}).
[c] Time elapsed to reach to T_{max}.

the time elapsed to reach to T_{max} was increased, i.e., the rate of the polymerization was decreased (Fig. 2). However, the reaction yield remained quantitative up to about 50 wt % of the used comonomer, then it dropped as the comonomer wt % increased. Again, no certain trend was observed in the M_n and PDI versus the comonomer increase.

As indicated in the literature,[4] αMeSt is more reactive than styrene as much as 10 to 100 times. But, reactivities of carbocations follow precisely the opposite direction (Scheme 3).

Because propagation is the reaction between a carbocation and monomer, both mentioned effects cancel one another and give similar rate constants for carbocationic propagation for most monomers. If this is true, then what about the certain trend of the overall polymerization rate observed in the present experiments (Fig. 2)? The observed trend is attributed to the equilibria between dormant and active species .

$$\text{Active} \underset{}{\overset{K_I}{\rightleftharpoons}} \text{Dormant} \quad (7)$$
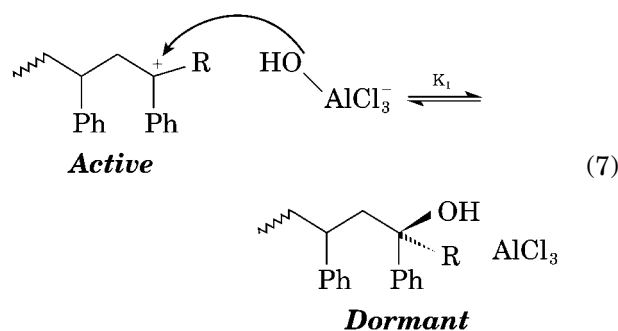
In this case the apparent rate constant of propagation is the product of the rate constant of prop-

agation (weakly depending on monomer structure) and the ionization constant [$k_{p(app)} \approx k_p \cdot K_I$].[14] This equilibrium constant is much lower for more stable cations derived from αMeSt than from styrene.

Although the study on copolymer composition was far from the scope of the present work, so much is certain that it is much more difficult to randomly copolymerize monomers by an ionic mechanism than by a free radical, due to the very strong substituent effects on the stability of carbanions and carbenium ions, and therefore on the reactivities of monomers. In addition, because the position of the equilibria between active and dormant species [eq. (7)] depends on solvent, temperature, activator, and structure of the active species, the reactivity ratios obtained from carbocationic copolymerizations are not reproducible.[4]

Lack of certain trends in the variation of MW and PDI versus the comonomer wt % (Table IV) may be explained through the same approach for the same factors mentioned under the "monomer concentration" title.

Solvent Practical Evaluation

From a practical viewpoint, the best available, less expensive, less toxic, and medium volatile solvent able to dissolve and/or disperse the catalyst was to be determined. Thus, kerosene, kerosene-toluene and kerosene-xylene mixtures, xylene, n-heptane, dichloromethane, and dichlo-
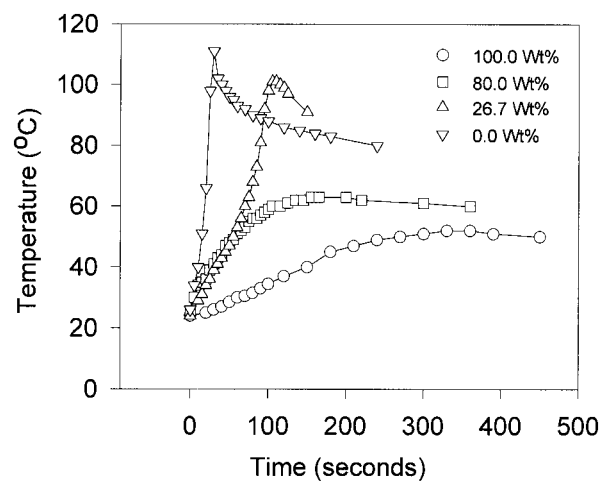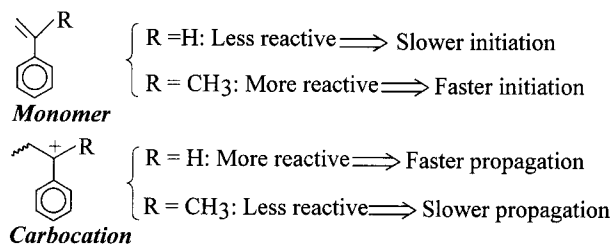

Figure 2 Variation of temperature versus time of reaction corresponding to the comonomer wt % of 0.0, 26.7, 80.0, and 100.0, leading to the yield of 100, 100, 85, and 61%, respectively.

Scheme 3

romethane-toluene mixture were evaluated. The results are summarized in Table V.

Kerosene as a cheap, available, plentiful, and nontoxic solvent having high flash point, was first examined. In the first batch (no. 78, no data given in Table V) of this series of experiments, the amounts of the reactants were chosen as the same of those performed in toluene (the optimum amounts: $AlCl_3$ 0.4 wt %, styrene 34 wt %). The catalyst particles' color was changed into orange as soon as contacting with kerosene, and then strongly agglomerated to form sticky soft lumps that adhered the internal wall of the reactor. This great deficiency (which actually removed the catalyst particles from the reaction) was tried to be eliminated by increasing of the catalyst and the monomer concentration (batch nos. 79 and 81), by increasing the catalyst only (batch no. 80), and also by using the solvent mixtures (batch nos. 82–84). Although the latter approach, including the addition of the monomer-kerosene solution into the well-dispersed catalyst in toluene or xylene, led to improved results (Table V), it was not recognized as an acceptable method. Kerosene has a wide boiling range (from ~140°C to above 250°C), therefore, complete removing of the residual solvent, even under longer periods at higher temperatures and vacuum, was practically impossible, so that the final resins had an unpleasant odor. Moreover, heating for removing the residual solvent was led to MW increasing and darker colors (see the next section; postheating).

Xylene (mixtures of isomers), in spite of its higher bp (~140°C), was found to be as a proper alternative to toluene (batch no. 85). In n-heptane (bp 98°C, d 0.68 g/cm^3), the catalyst was very well-dispersed but completely insoluble (in contrast to toluene or xylene, which sparingly dissolve the catalyst). Therefore, the reaction temperature increase was taken as long as 12 min to reach to T_{max}. In fact, the reaction improving was limited by lack of the effective collision of the monomer and the catalyst particles. The final

yield was decreased due to high density difference of the resin and the solvent.

Dichloromethane was the only polar solvent evaluated in this part of the work. It led to favorable results, either alone (batch no. 97) or with accompanying of toluene (batch no. 98). These synthesized colorless (Gardner scale < 1) solid products that can be easily ground (as white powders) or flaked may be considered as high-quality tackifying resins. As a result, CH_2Cl_2 or CH_2Cl_2/toluene was recognized to be a very good alternative to toluene. The effects of the solvents nature on the polymerization and the resin characteristics are under investigation in this laboratory.

Postheating

A preliminary study was performed to elucidate the effect of the thermal treatment on the resins during the last purification step (heating period; experimental section). Thus, two synthesized resins, as well as two commercial aromatic resins were heated at 110°C in an air-circulating oven for 18 h. The results are given in Table VI.

All the thermal posttreated samples showed higher molecular weight and narrower molecular weight distribution (lower PDI) as compared with the corresponding samples before heating. Order of the M_n increasing as a result of the heat treatment was as: no. 61>no. 49>>Petro>Colon. The observation may be attributed to thermal reactions between the limited unsaturated sites in
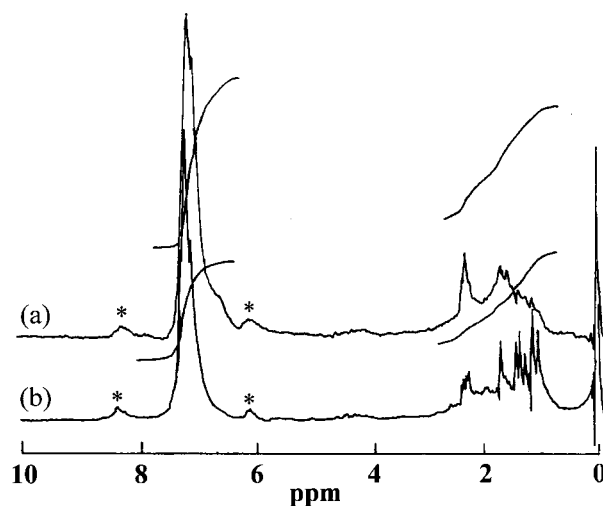

Figure 3 Representative NMR spectra of (a) a wholly styrenic and (b) a styrene-αMeSt tackifying resin (no. 63). Asterisk indicates side bands arose from unsuitable rotational speed of the NMR sample tube.

Table V Results of Qualitative Study[a] to Evaluate the Most Applicable Solvent, and the Solvent Effects on the Resins Specifications (Starting Reaction Temp., 25°C)

Batch No.	Solvent	T_{max} (°C)	Yield (%)	Resin Color	M_n	PDI
79[b]	KER[c]	53	88	Yellow, opaque	1494	2.27
80[d]	KER	151	94	Dark brown	1046	2.88
81[e]	KER	65	56	Dark yellow	—	—
82[f]	KER/PhMe (1 : 2 v/v)	135	~100	Light yellow	1468	1.94
83[d]	KER/PhMe (1 : 2 v/v)	73	72	Light yellow	1511	2.11
84[d]	KER/Xylene (2 : 5 v/v)	145	95	Yellow, opaque	1182	2.20
85[g]	Xylene	120	99	Light yellow	1090	2.22
86[h]	n-Heptane	101	80	Yellow, opaque	1249	2.23
97[i]	CH_2Cl_2	44	~100	Colorless	1211	3.07
98[i]	CH_2Cl_2/PhMe (1 : 1 v/v)	67	~100	Colorless	1603	1.47

[a] Base amounts of common reactants are $AlCl_3$ = 0.4 wt %, styrene = 34 wt %, unless otherwise mentioned.
[b] The solvent volume was reduced to half.
[c] Kerosene.
[d] Catalyst 0.8 wt %.
[e] Catalyst 0.8 wt %; monomer 17 wt %.
[f] Catalyst 1.6 wt %.
[g] The pure monomer was added to the catalyst dispersion.
[h] The product was settled down as a heavy oil, separating into two phases. The end product was solid. See experimental section for more details.
[i] Product was a solid resin. See experimental section for details.

some chains (see Scheme 2), leading to higher MW, especially in the case of the αMeSt-contained resin (no. 61), which is expected to include more such sites.[14] On the other hand, weight loss of the synthesized samples (nos. 49 and 61) was much higher than that of the commercial resins. The weight loss may arise from the elimination of lighter oligomeric components having enough volatility to remove under heating. Comparison of the thermal and physical properties of the resins is under investigation in this department.

Characterization

In addition to determination of MW and MW distribution of the resin by GPC, their molecular structure was confirmed by IR and NMR spectroscopy. All the IR spectra were almost the same of those of standard polystyrene,[19] due to similarity of their structure. The strong bands at 700 cm^{-1} and 760 cm^{-1} are particularly characteristics of the mono-substituted benzene rings as are the combination variations between 1950 cm^{-1} and 1650 cm^{-1} (finger bands). In homopolymer resins, the band at 1370 cm^{-1} (medium), 1328 cm^{-1} (very weak), and 1183 cm^{-1} (weak) belong to wagging and twisting vibrations of the CH_2 groups.

In copolymeric resins, the substitution of the α-hydrogen atom in the chain by CH_3 is only evident in the additional presence of the methyl group vibrations[19]: asymmetric stretching at 2970 cm^{-1} (very strong), asymmetric bending at 1472 cm^{-1} (strong), symmetric bending at 1378 cm^{-1} (medium), and rocking vibration at 947 cm^{-1} (very weak). The vibrations of the tertiary H atom are masked by other bands, so it is not possible to observe their appearance. On the other hand, there are two additional medium to weak bands at 1310 cm^{-1} and 1280 cm^{-1}. Assignments of these peaks are a subject of debate.

In NMR spectra, two absorption peak regions were observed: aromatic protons at 6.5–7.7 ppm and aliphatic protons at 0.7–2.8 ppm (Fig. 3). No another band was observed in other regions of the spectra. So, all the resins had no considerable olefinic unsaturation. Although the resins from pure

Table VI Effect of Thermal Posttreatment on Some Aromatic Tackifying Resins (110°C, 18 h)[a]

Resin	M_n (Bh)	M_n (Ah)	PDI (Bh)	PDI (Ah)	Weight Loss (%)
No. 49	1159	1429	1.82	1.73	15.1
No. 61	1213	1833	1.77	1.41	16.8
Colon[b]	829	859	3.30	1.95	0.4
Petro[c]	1029	1086	2.60	2.30	0.7

[a] M_n and PDI values obtained from GPC (in THF, 30°C); Bh = before heating, Ah = after heating.
[b] Colon P-120 (pale yellow; softening point 120°C; DSC: T_m = 91.0°C, no T_g observed), produced by Colon Chem. Co. Ltd., Japan.
[c] Petro-Rez 300 (pale yellow; softening point 100°C; DSC: T_m = 88.4°C, no T_g observed), produced by Akrochem Corp., USA.
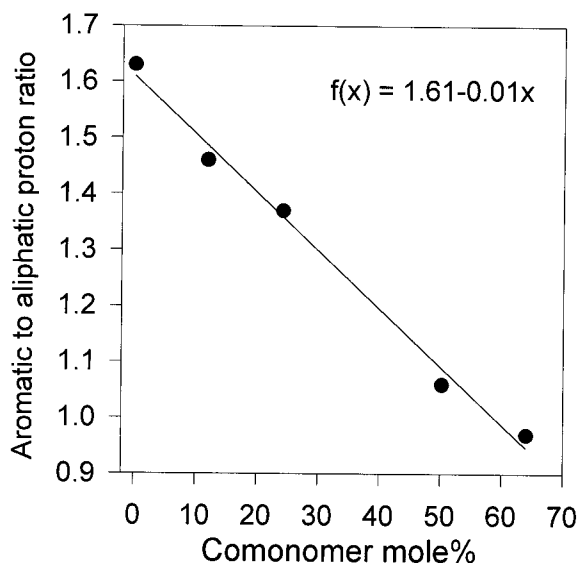
Figure 4 Plot of aromatic to aliphatic proton ratio (obtained from NMR peak area) versus mole percent of αMeSt.

monomers are known as well-defined structured macromolecules,[4] the various species formed in the carbocationic polymerization (Scheme 2) could not clearly elucidate by low-resolution NMR. However, the proportion of aromatic to aliphatic protons may be used in identifying composition of αMeSt-contained resins. Because the polymerization yields for the synthesized resins obtained from batch nos. 48 and 60 to 64 were measured to be quantitative (Table IV), it may be accurately assumed that the composition of each of these (co)polymers are the same as for the corresponding feeds. Therefore, a linear plot presenting ratio of aromatic to aliphatic hydrogen peak area versus αMeSt mol % can be drawn (Fig. 4). This plot may simply be applied to quantify comonomer composition of the similar copolymers if the copolymerizations give quantitative yields. The plot was tested with the resin no. 62 as an assuming unknown copolymer. The aromatic to aliphatic proton peak area for this sample was measured from its NMR spectrum to be 1.24. Thus, the αMeSt composition in the resin was graphically measured to be 37.0 mol %, which is comparable with the same as true feed composition of the comonomer for this resin; i.e., 37.2 mol %. Generally, the application of the plot may be extended to estimate comonomer composition in any poly(styrene-*co*-αMeSt) resin, apart from preparation method, molecular weight, and polydispersity.

CONCLUSION

Low-molecular-weight styrenic polymers (technical pure-monomer-based tackifying resins) were synthesized using cationic (co)polymerization through an incremental monomer addition procedure. Certain parameters affecting on the reaction and on the resins characteristics, i.e., starting reaction temperature, catalyst, monomer, and comonomer (αMeSt) concentration, and type of the reaction solvent were investigated. The main conclusions may be summarized as the following:

1. Quantitative yields were obtained using 0.3 wt % of $AlCl_3$ and more (Table I), so, 0.4 wt % of the catalyst was chosen as an optimized concentration to ensure achieving quantitative yield.
2. Broader MW distribution obtained when the starting temperature of the reaction was 0°C instead of 20°C (Table I).
3. Lower starting temperatures gave lighter-colored resins (Table II). Therefore room temperature (25°C) was chosen as a proper starting reaction temperature.
4. The monomer concentration of ~35 wt % was recognized to be the optimum amount lead to highest yield, wherein the catalyst to monomer weight ratio was 0.02 (Table III).
5. Rate of polymerization was decreased with increasing of αMeSt concentration (Table IV, Fig. 2).
6. No certain trend was observed in the variation of M_n and PDI versus concentration of the monomer and the comonomer (Tables III and IV).
7. Although the rate of polymerization was decreased with increasing of the comonomer wt %, the reaction yield was remained quantitative up to ~50 wt % of the comonomer used (Table IV).
8. Xylene, CH_2Cl_2, and CH_2Cl_2/toluene were recognized to be good alternatives to toluene as the polymerization solvent (Table V).
9. Thermal post-treatment caused M_n increase and PDI decrease either in styrenic or in commercial aromatic resin samples (Table VI).
10. A linear plot of the ratio of aromatic to aliphatic protons peak area (obtained from the NMR spectra of the synthesized copolymeric

resins) versus αMeSt mol % was proposed to apply for estimating the comonomer composition in all similar copolymeric resins.

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