

Shi-Fa Wang · Takeshi Furuno · Zhi Cheng

## Studies on the synthesis and properties of terpene-phenol-aldehyde resin with a high softening point

Received: February 12, 1999 / Accepted: June 4, 1999

**Abstract** Synthesis conditions of terpene-phenol-aldehyde resin with a high softening point were studied based on the reactions among  $\alpha$ -pinene, phenol, and formaldehyde. A suitable catalyst system and the best processing conditions were obtained by laboratory experiments. The influence of the raw materials ratios, reaction temperature, reaction time, and catalyst dose on the softening point, yield, and color of the synthesized resin was examined. The physical and chemical characteristics of the resin were determined: softening point  $\geq 140^\circ\text{C}$  (ball and ring method); color value  $\leq 7$  (Gardner); acid value (KOH mg/g)  $< 1$ ; bromine value ( $\text{Br}_2$  mg/100 g)  $< 64$ ; saponification value (KOH mg/g)  $< 1$ ; average molecular weight  $\sim 830$ . The yield of resin was more than 85% (based on the total raw material).

**Key words**  $\alpha$ -Pinene · Phenol · Formaldehyde · Polymerization · Condensation

### Introduction

Terpene-phenol-aldehyde resin, a co-polymer product obtained by cationic co-polymerization of monoterpene with phenol and aldehyde, is a new modified phenolic aldehyde resin. It is transparent, light yellow material that is soluble in most solvents and is compatible with rubber, rosin, and others.<sup>1</sup> It is useful as an adhesive, serving as a tackifier. In coatings it increases the hardness of the coating, and drying is accelerated.<sup>2</sup> The resistance of window sealing tape to sag and heat flow is enhanced by adding terpene-phenol-formaldehyde resin.<sup>3</sup> The resin can be used to make a sealant

that has excellent adhesive deformation properties and long-term stability.<sup>4</sup> Phenolic resin modified with terpene can also be made into an aqueous emulsion that shows good stability during storage at  $20^\circ\text{C}$ . Veneer plates laminated with the emulsion show good shear strength.<sup>5</sup> In addition, the resin can be used in other fields, such as in polyurethane foam, printing ink, and shoe making.<sup>6,7</sup>

The terpenes usually used for the synthesis of terpene-phenol-aldehyde resin are  $\alpha$ -pinene,  $\beta$ -pinene, limonene, carene, camphene, and others. The phenols used are phenol, 3,4-dimethylphenol, 4-methylphenol, and others. The aldehyde used is mainly formaldehyde.

There are two methods for synthesizing the resin. With the first method, phenol is condensed with aldehyde in the presence of an acidic catalyst and is then alkylated with terpene in the presence of Lewis acid or protonic acid.<sup>8,9</sup> With the second method, phenol is first polymerized with terpene in the presence of an acidic catalyst and is then condensed with the formaldehyde.<sup>10</sup> Up to now, the terpene-phenol-aldehyde resin produced with these methods has had a low softening point (softening point at less than  $100^\circ\text{C}$ ) and a deep color. There have been few reports on the synthesis of terpene-phenol-formaldehyde resin with a high softening point.

The main purpose of the present study was to synthesize the terpene-phenol-aldehyde resin with a high softening point and a light color from turpentine produced in China (in China the main source of terpene is turpentine, of which the main component is  $\alpha$ -pinene), phenol, and formaldehyde and to determine the suitable reaction conditions.

### Materials and synthesis method

#### Materials

Turpentine obtained from the Fujian Forest Chemical Engineering Factory was fractionally distilled, and  $\alpha$ -pinene with a purity of 98% was produced. Formalin (formaldehyde content 37%), phenol, and other reagents were all of analytical grade.

S.-F. Wang · T. Furuno (✉)  
Faculty of Science and Engineering, Shimane University, Matsue  
690-8504, Japan  
Tel. +81-852-32-6563; Fax +81-852-32-6123  
e-mail: t-furuno@riko.shimane-u.ac.jp

Z. Cheng · S.-F. Wang  
College of Chemical Engineering of Forest Products, Nanjing  
Forestry University, Nanjing 210037, China

## Synthesis method

Comparing the two synthesis methods, the second one is better because the resin produced by the first method has a deep color before being decolorized, a low softening point, and low yield. It is difficult to remove the decolorizer by filtering if the decolorizer is added to the reaction liquid because of the high viscosity of this liquid. In contrast, the resin produced by the second method has a higher softening point and a lighter color. In addition, the yield of resin is somewhat higher than that of the first method. Hence, the second protocol was chosen to synthesize the resin. The simple process is shown in Fig. 1.

The synthesis of resin was carried out in a round-bottomed flask with four necks in which a stirrer, a thermometer, and a reflux condenser were fixed. The polymerization reaction was completed in a 0.5-l round-bottomed flask. A waterbath was used to control the reaction temperature.  $\alpha$ -Pinene, phenol,  $\text{BF}_3\text{-C}_2\text{H}_6\text{O}$  (catalyst-1), and solvent were added to the flask, and the reaction was carried out under the predetermined temperature and time. Hot water or alkali was added to the reactants to break off the reaction, and the reactants were washed with water until reaching neutrality (determined with pH test paper). The water was separated from the organic phase. The organic phase obtained after washing was further reacted with formaldehyde in the presence of trichloroacetic acid (catalyst-2). The reactants were also washed with water until reaching neutrality. The washed reactants were first distilled at normal pressure to remove the solvent and the unreacted raw material; then they were further distilled at

high vacuum (0.099Mpa) to remove the oligomer, and the products were obtained.

## Determination of the main quality indexes of terpene-phenol-aldehyde resin

The items determined were the softening point, acid value, saponification value, bromine value, color value, and average molecular weight of the resin. The latter was determined by gel permeation chromatography (GPC) using Waters HPLC/GPC. Two columns (Waters 500A and 100A) were used by series connection. The average molecular weight of the resin was calculated with Waters Data Module. The softening point and the color value were determined with the ball-and-ring and Fe-Co methods, respectively.<sup>11</sup> A solution of  $\text{KOH-C}_2\text{H}_5\text{OH}$  was used to determine the acid value and the saponification value.<sup>11</sup>

## Results and discussion

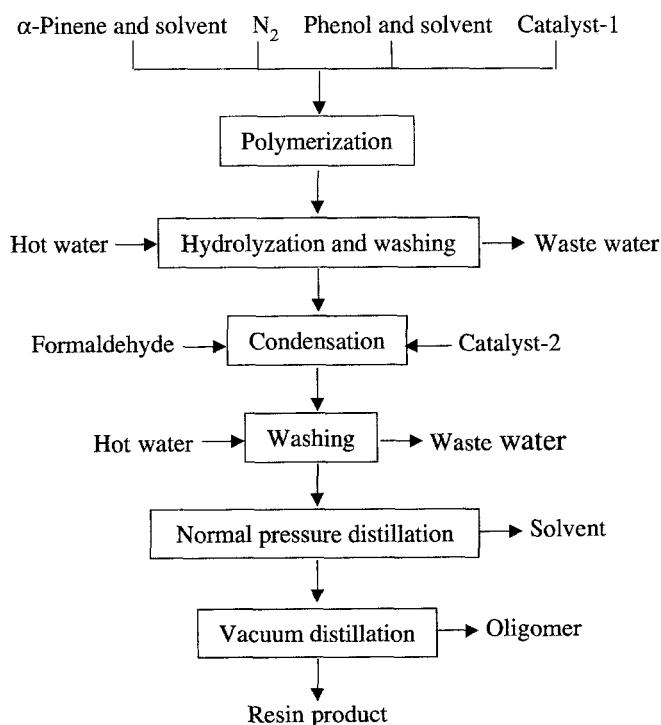
### Main factors influencing the synthesis of $\alpha$ -pinene-phenol-formaldehyde resin

During the synthesis process it was found that polymerization and condensation are key steps because the color, softening point, and yield of resin are influenced directly by them. The polymerization conditions of  $\alpha$ -pinene with phenol have also been studied.<sup>12</sup> In the present study, the main purpose was to probe the suitable condensation conditions for obtaining the resin with a high softening point and a light color.

### Influence of the $\alpha$ -pinene/phenol/formaldehyde molar ratio on the characteristics of the resin

The molar ratios of the reactants greatly affect the yield, softening point, and color of the resin. The experimental results are shown in Table 1.

It was found that the molar ratios of reactant directly affected both the yield and the softening point of the resin. When the  $\alpha$ -pinene/phenol ratio was 1.0:0.6, the yield and the softening point were improved along with the change in the phenol/formaldehyde ratio, from 1.0:0.9 to 1.0:0.8.



**Fig. 1.** Flow diagram for the operation of synthesizing resin. Catalyst-1,  $\text{BF}_3\text{-C}_2\text{H}_6\text{O}$ ; Catalyst-2, trichloroacetic acid

**Table 1.** Influence of the ratios of reactants on the yield, softening point, and color of resin

MR (mole)	Y (%)	SP (°C)	C (Gardner)
1.00:0.60:0.54	67	142	7
1.00:0.60:0.48	85	144	7
1.00:0.60:0.42	84	145	7
1.00:0.60:0.36	86	136	7
1.00:0.50:0.50	84	134	7
1.00:0.50:0.45	90	126	6
1.00:0.50:0.40	86	123	7

MR, molar ratio of  $\alpha$ -pinene:PhOH:HCHO; Y, yield of resin; SP, softening point of resin; C, color value of resin

They were relatively steady when the phenol/formaldehyde ratio was in the range of 1.0:0.8 to 1.0:0.7, but the softening point decreased at a phenol/formaldehyde ratio of more than 1.0:0.7. When the  $\alpha$ -pinene/phenol ratio increased from 1.0:0.6 to 1.0:0.5, the yield of resin hardly varied, whereas its softening point was obviously reduced. In contrast, the color of the resin deepened when the  $\alpha$ -pinene/phenol ratio was less than 1.0:0.6. Based on these results, the suitable reactant  $\alpha$ -pinene/phenol/formaldehyde ratio ranged from 1.00:6.00:0.36 to 1.00:0.60:0.48.

#### Influence of various catalysts on resin characteristics

$\alpha$ -Pinene could be polymerized with phenol in the presence of Lewis acid or proton acid (e.g.,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BF}_3\text{-HOAc}$ ,  $\text{BF}_3\text{-(C}_2\text{H}_5)_2\text{O}$ ,  $p\text{-MeC}_6\text{H}_4\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_3$ ) or in the presence of a strong acidic cationic exchanger (e.g., Lewatit SPC 108/H). Each catalyst had a different effect. Among them,  $\text{BF}_3$  had a good catalytic effect. A resin with a high softening point could be produced in the presence of  $\text{BF}_3$ , although the color of the obtained resin was a little deep without the presence of antioxidant or decolorizer. Zinc dust could be used with chalk as an antioxidant,<sup>1</sup> but the chalk was difficult to remove by filtering, and the transparency of the resin was not good. This study showed that several methods could improve the color of resin: when a little ammonia or iodine was added to the reactants at the beginning of the distillation process, the reactants were protected with  $\text{N}_2$  or  $\text{CO}_2$  during the reaction and distillation. Therefore,  $\text{BF}_3$  was selected as the catalyst for the polymerization.

Alkali and acid could be used as the catalyst for the condensation reaction of  $\alpha$ -pinene/phenol prepolymer with formaldehyde. The catalytic effects of the various catalysts are shown in Table 2.

It was found that trichloroacetic acid (TCA) was the best catalyst because the yield and softening point of resin were rather high and the color was not deep. The influence of TCA dose on the yield, softening, and color of resin is shown in Table 3. The test results showed that the TCA

**Table 2.** Influence of various catalysts for the condensation reaction on the yield, softening point, and color of resin

CA	Y (%)	SP (°C)	C (Gardner)
TCA			
3	90.5	127	7
5	85.7	143	7
$\text{H}_3\text{PO}_4$			
3	88.0	118	6
5	87.8	122	5
NaOH			
3	88.5	139	10
5	87.2	154	11
HCl			
3	83.0	123	10
5	82.0	124	11

CA, catalyst and dose (weight percent based on total raw material); Y, yield of resin; SP, softening point of resin; C, color value of resin; TCA, trichloroacetic acid

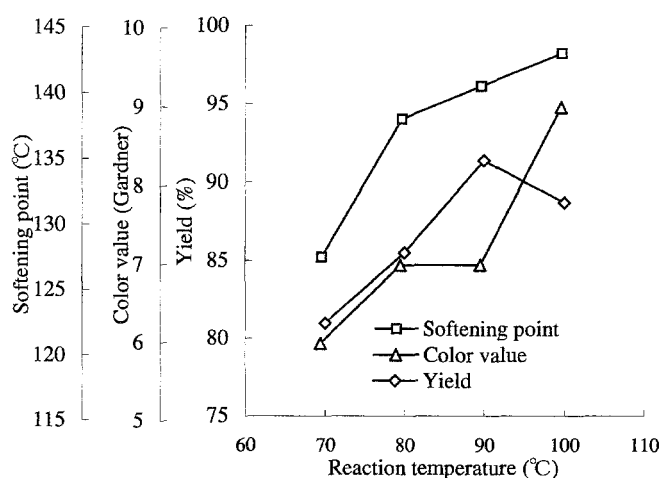
dose had an important influence on the characteristics of the resin. The color deepened at a TCA dose of more than 7.0%. In contrast, the softening point and yield were somewhat low at a TCA dose of less than 1.0%, and the reaction rate was slow. Hence, the suitable TCA dose was 3.0%–5.0%.

#### Influence of the condensation reaction temperature on the yield, softening point, and color of resin

Figure 2 shows that the temperature of the condensation reaction greatly influenced the resin characteristics. When the temperature was below 90°C, the yield and softening point increased as the reaction temperature rose. On the other hand, the color of the resin deepened with the increased reaction temperature and was obviously deepened when the temperature was over 90°C. A suitable temperature was 80°–90°C.

#### Influence of the length of the condensation reaction on the yield, softening point, and color of resin

The duration of the condensation reaction consisted of two parts: the “dropping time” of the reactants and the constant temperature duration. TCA was first mixed with formaldehyde, and the mixture was dropped into the reaction



**Fig. 2.** Influence of reaction temperature on the yield, softening point, and color of resin

**Table 3.** Influence of trichloroacetic acid doses on the yield, softening point, and color of resin

TCA (%)	Y (%)	SP (°C)	C (Gardner)
1.0	84.0	134.0	7
3.0	90.5	136.5	7
5.0	85.7	145.5	7–8
7.0	84.3	139.0	9–10

Y, yield of resin; SP, softening point of resin; C, color value of resin; TCA, trichloroacetic acid

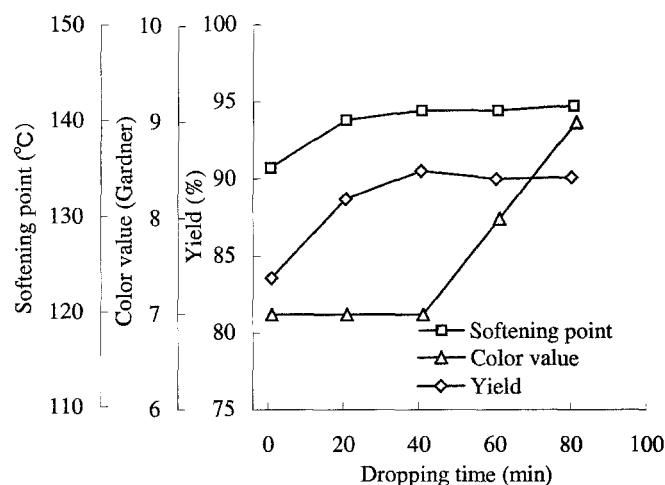


Fig. 3. Influence of dropping time of formaldehyde and catalyst on the yield, softening point, and color of resin

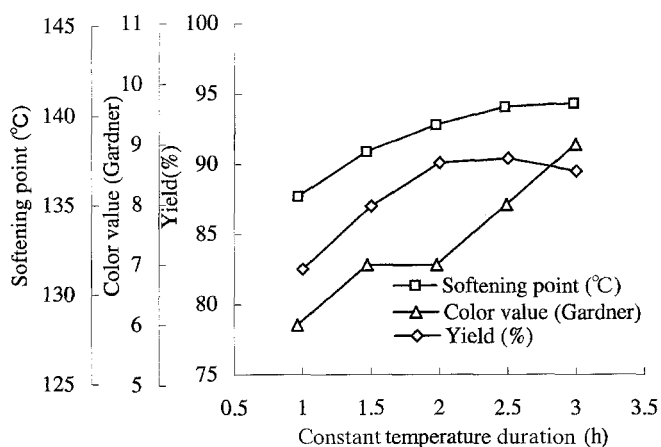


Fig. 4. Influence of constant temperature duration of the condensation reaction on the yield, softening point, and color of resin

mixture of  $\alpha$ -pinene and phenol. The experimental conditions were as follows: the  $\alpha$ -pinene/phenol/formaldehyde molar ratio was 1.00:0.60:0.48; the reaction temperature was 80°–90°C; and the TCA concentration was 4%. The test results are shown in Fig. 3. The yield and softening point of resin increased slightly as the dropping time was prolonged. When the dropping time was more than 40 min, the yield and softening point did not increase, but the color deepened slowly. The suitable dropping time was 20–40 min.

The influence of the constant temperature duration on the yield, softening point, and color is shown in Fig. 4. The yield and softening point increased with prolongation of the constant temperature duration. At a constant temperature duration of 2 h, the yield was the highest and the softening point reached about 140°C. The yield and softening point hardly increased after 2 h. The color of the resin deepened with prolongation of the constant temperature duration. A suitable constant temperature duration is 1.5–2.0 h.

The total time of the condensation reaction was determined on the basis of the dropping time and constant

Table 4. Influence of distillation temperature on the characteristics of the resin

Dt (°C)	Y (%)	SP (°C)	C (Gardner)
230–240	100	120	9
250–260	95	131	8
270–280	90.5	142.5	7
290–300	83	143.5	9

Dt, distillation temperature; Y, yield of resin; SP, softening point of resin; C, color of resin

Table 5. Main factors and test results

Test no.	Main influence factors				Test results		
	MR (mole)	CA (%)	RT (°C)	KT (h)	Y (%)	SP (°C)	C (Gardner)
1	1:0.6:0.48	1	80	1.5	88.1	130.0	7
2	1:0.6:0.48	3	85	2.0	85.6	143.8	7
3	1:0.6:0.48	5	90	2.5	80.0	147.0	8
4	1:0.6:0.42	1	85	2.5	82.2	145.0	7
5	1:0.6:0.42	3	90	1.5	82.1	141.6	8
6	1:0.6:0.42	5	80	2.0	84.0	138.8	7
7	1:0.6:0.36	1	90	2.0	81.0	132.0	8
8	1:0.6:0.36	3	80	2.5	83.4	126.0	7
9	1:0.6:0.36	5	85	1.5	84.0	129.4	8

MR, molar ratio of  $\alpha$ -pinene:PhOH:HCHO; CA, dose of organic acid catalyst; RT, reaction temperature; KT, keeping time; Y, yield of resin; SP, softening point of resin; C, color value of resin

temperature duration. A suitable total reaction time was 2.0–2.5 h, and that of the dropping time was about 0.5 h.

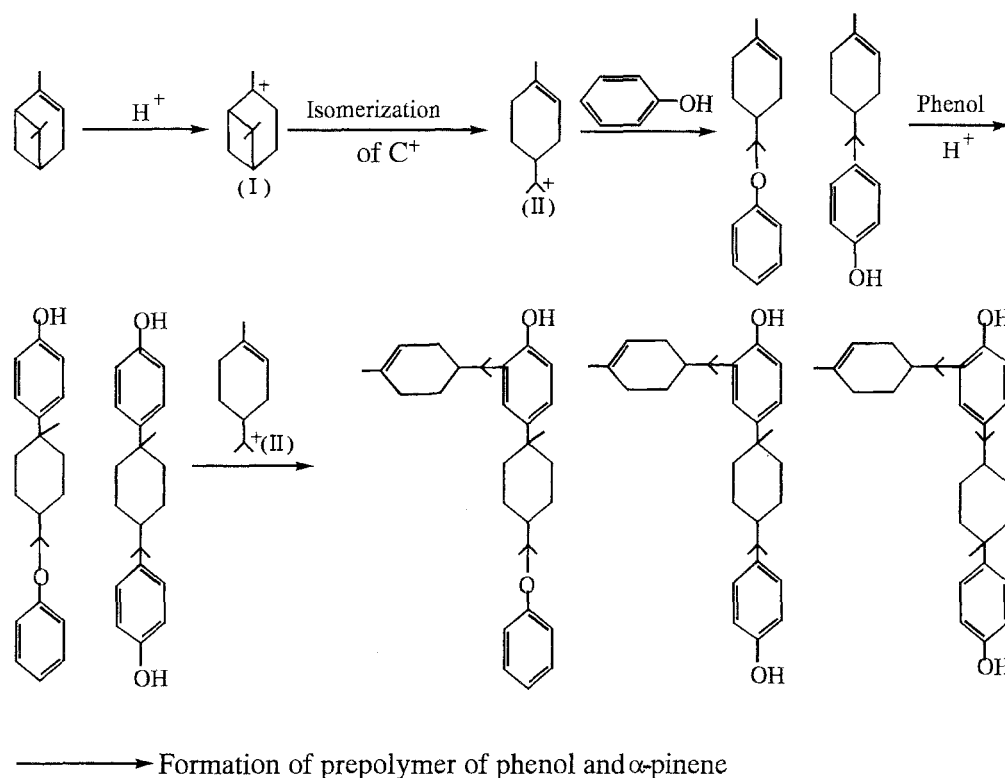
#### Influence of distillation condition on resin characteristics

Under the same reaction conditions, the distillation temperature influenced the characteristics of the resin, especially its yield and softening point, as shown in Table 4. The yield decreased and the softening point increased with an increasing distillation temperature. At a distillation temperature of more than 270°–280°C, the softening point hardly changed but the yield significantly decreased. The probable reason was that some of the oligomer was distilled away. At a distillation temperature of 270°–280°C, the softening point reached 142.5°C and the yield was more than 90%. Therefore, a suitable distillation temperature was 270°–280°C.

#### Optimum technological conditions for the condensation reaction

To reduce the mutual influences among various factors and to obtain the best synthesis conditions, the experimental conditions were further refined by means of the orthogonal test. The factors chosen were the raw materials ratio, reaction temperature, reaction time, and the dose of catalyst-TCA for the condensation reaction. These factors, their levels, and the test results are outlined in Table 5. The

**Fig. 5.** Formation of the prepolymer of phenol and  $\alpha$ -pinene



results of the analysis of variance (ANOVA) showed that the reaction temperature had the greatest influence on the qualities of resin. The next most important factor was the reaction time. The catalyst dose and the reactant ratios had less influence. Based on the results of the ANOVA, the optimum technological conditions for the condensation reaction were as follows: The  $\alpha$ -pinene/phenol/formaldehyde molar ratio was 1.00:0.60:0.42–0.48, the reaction temperature was 90°C, the condensation reaction time was 2.0h (including the dropping time of 30 min), and the TCA concentration was 3% (based on the total weight of the reactants). The main quality indexes of resins synthesized under optimum conditions are shown in Table 6. The appearance of the synthesized resin was a light yellow, fragile solid. The resin was soluble in benzene, toluene, xylene, and other organic solvents; but it was not soluble in water.

Probable reaction mechanism for the polymerization and condensation among  $\alpha$ -pinene, phenol, and formaldehyde

Based on the phenomena occurring during the course of the experiments, the probable mechanism of the reaction is as follows: As shown in Fig. 5,  $\alpha$ -pinene first caused the isomerization reaction in the presence of Lewis acid, and  $C^+$ -I and  $C^+$ -II were formed. Then the  $C^+$ -II attacked the phenol as an electrophilic reagent. The electrophilic substitution reaction took place on the benzene ring, and the carbon-carbon links were formed. The  $C^+$ -II mainly attacked the para-position of phenol because of the steric resistance. In the meantime, a part of the  $C^+$ -II cation also attacked the oxygen atom of the phenolic hydroxyl, and

**Table 6.** Main quality indexes of the synthesized resin

Characteristics	Quality index
Softening point (ball and ring, °C)	$\cong 140$
Color value (Gardner)	$\leq 7$
Acid value (KOH mg/g)	$< 1$
Saponification value (KOH mg/g)	$< 1$
Bromine value (Br mg/g)	$< 64$
Average molecular weight	$\sim 830$

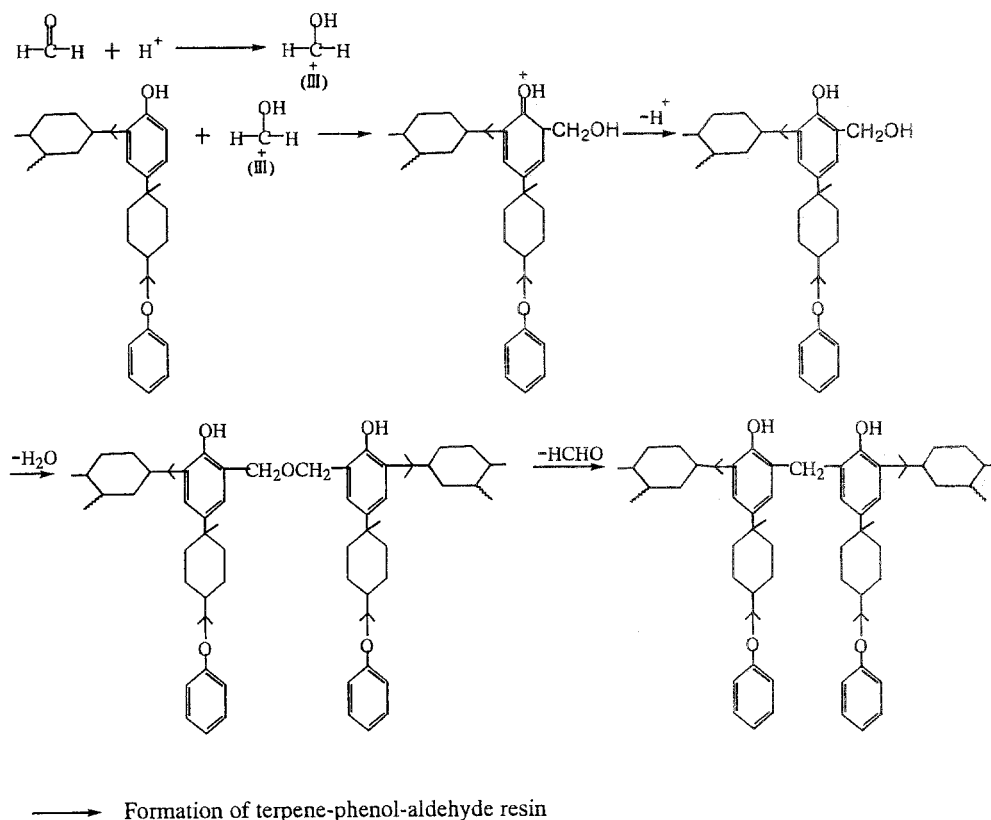
ether links were formed. Therefore, the prepolymer of  $\alpha$ -pinene with phenol was formed by two kinds of link.

As shown in Fig. 6, in the presence of catalyst the prepolymer of  $\alpha$ -pinene and phenol could react further with formaldehyde. Formaldehyde first combined with  $H^+$  ions, and  $C^+$ -III was formed.  $C^+$ -III attacked the unreacted ortho- and para-positions of the phenol. Hydroxymethyl was formed on the phenol cycle.  $H_2O$  (1 mol) was dehydrated between two hydroxymethyl groups on the different two molecules. Thus the resin was formed.

## Conclusions

Terpene-phenol-aldehyde resin with a high softening point and light color was synthesized by the reaction among  $\alpha$ -pinene, phenol, and formaldehyde. The main factors (e.g., reaction temperature, reaction time, catalyst dose, and the ratio of the raw materials) affected the yield, softening

**Fig. 6.** Formation of  $\alpha$ -pinene-phenol-formaldehyde resin by the further reaction of formaldehyde with the prepolymer of phenol and  $\alpha$ -pinene



point, and color of the resin. The reaction temperature was the most important of the various factors, and it had a great influence on the color of the resin. The optimum technological conditions for the condensation reaction were determined: the  $\alpha$ -pinene/phenol/formaldehyde molar ratio 1.00:0.60:0.42–0.48; the reaction temperature 90°C; reaction time 2 h (including the dropping time of 30 min); concentration of the catalyst 3.0%; and distillation temperature 270°–280°C.

## References

- Mamfred G, Karl H (1976) Terpene-phenol resins. Ger Offen 2,616,592, October 28, 1976
- Gajduchenya Galina M, Kirasirova Valentina N (1993) Formaldehyde-phenol-terpene resin coatings (in Russian). Izobreteniya 5:56
- Rizzer Alexander J (1973) Composition of sealing joint. US 3,759,780, September 18, 1973
- Bublik AT, Vlasov VI, Gavrilushkina FS, Zhukova AF, Kreindel MY, Kuprina LB, Nesterova ET, Nesterov AS (1988) Sealing compound (in Russian). Otkrytiya Izobret 14:118
- Sasaki T, Noguchi K (1994) Terpene-modified phenol resin aqueous emulsion compositions (in Japanese). Jpn Kokai Tokkyo Koho JP 08,100,104, April 16, 1994
- Boutillier J, Dehay G, Forichon N, Leroux R (1986) Assembling surfaces by applying a polyurethane or polyether amide joint, superficially melting this joint and cooling it. Eur Pat Appl EP 197,845, October 15, 1986
- Nesterova ET, Kuprina LB, Borovkova NN (1985) Production of terpenic phenol-formaldehyde resin from monoterpene hydrocarbons (in Russian). Gidroliz Lesokhim Prom-st 1:15–16
- Fukui T, Sakamoto T, Fujita N (1979) Manufacture of phenolic resins (in Japanese). Jpn Kokai Tokkyo Koho 79,116,080, September 10, 1979
- Yurasov PF, Zyuzyun VE (1984) New type of products at the Verkhoture Wood-chemical Plant (in Russian). Gidroliz Lesokhim Prom-st 8:24–25
- Lin J, Ma CZ (1989) Synthesis of terpene-phenol-aldehyde resin (in Chinese). Sci Techn For Chem 3:23–25
- National standard of terpene-phenol resin (in Chinese). 1992
- Yuan YZ, Cheng Z (1989) Preparation of terpene phenolic resin (in Chinese). J Nanjing For Univ 13(1):22–31