

# Cationic Copolymerization of 1,3-Pentadiene with 1,3-Cyclopentadiene

YU XING PENG, HAN SONG DAI, LIN FENG CUN, JIA LIN LIU

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, P.O. Box 415, Chengdu 610041, People's Republic of China

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**ABSTRACT:** Copolymerizations of 1,3-pentadiene (PD) with 1,3-cyclopentadiene (CPD) initiated by aluminium trichloride were carried out in toluene. The addition of CPD in the PD polymerization system does not affect the molecular weight but greatly increases the softening point of the polymer due to the introduction of cyclic structures. The Gardner color scale of the polymer is also raised by introduction of unsaturated rings of CPD. The copolymerization gives a complete conversion but generates insoluble crosslinked gels at high CPD content due to the high crosslinking reactivity of CPD. The integral intensities of unsaturated protons from PD and CPD segments of the copolymer chain on the  $^1\text{H-NMR}$  spectrum give a perfect correlation with the copolymer compositions. The low-conversion experiments were carried out with small amounts of CPD in order to determine the reactivity ratio in this copolymerization system ( $M_1 = \text{PD}$  and  $M_2 = \text{CPD}$ ). The result of  $r_1 = k_{11}/k_{12} = 0.46$  demonstrates that CPD has a higher reactivity than PD toward PD growing carbocations, and hence the copolymer shows a higher CPD proportion than the corresponding comonomer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1883–1887, 1997

**Key words:** 1,3-pentadiene; 1,3-cyclopentadiene; cationic polymerization; copolymerization; reactivity ratio

## INTRODUCTION

The cationic polymerization of the  $\text{C}_5$  fraction comprising a variety of  $\text{C}_5$  diolefins and monoolefins is of increasing industrial importance in the production of aliphatic petroleum resins useful in various applications.<sup>1</sup> In this multicomponent polymerization system the feed composition is among the most important factors determining the structure and property of the polymer.<sup>2</sup> For example, the content of cyclic  $\text{C}_5$  olefins in the feed exerts a strong influence on the polymerization process and the ultimate property of the resin due to the introduction of cyclic structures in the lin-

ear polymer chain.<sup>1</sup> We recently became interested in the copolymerization of 1,3-pentadiene (PD) and 1,3-cyclopentadiene (CPD), the most important linear and cyclic dienes in the  $\text{C}_5$  fraction, respectively. It has been found that CPD shows a high cationic polymerizability in its homopolymerization<sup>3</sup> and the copolymerizations<sup>4</sup> with isobutylene and  $\alpha$ -methylstyrene. However, its cationic copolymerization with PD has never appeared in the present literature.

The present article concerns the PD–CPD copolymerization induced by  $\text{AlCl}_3$  in toluene, in which we describe our investigations on the polymer yield, the crosslinking reaction, the softening point, and the molecular weight of the polymer. In addition, the reactivity ratio of PD in this copolymerization system is determined and discussed.

Correspondence to: Y. X. Peng.

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## EXPERIMENTAL

### Materials

Commercial PD and CPD from Fluka were dried with  $\text{CaH}_2$  and distilled. The solvents were also distilled over  $\text{CaH}_2$ .  $\text{AlCl}_3$  was purified by sublimation in a vacuum.

### Polymerization

The polymerizations were carried out in a three-necked reactor in a dry nitrogen atmosphere. The solvent was introduced into the reactor first, then the initiator was added, and finally the comonomer was introduced with a syringe. Methanol-containing solvent was used to quench the polymerization. The reaction solution was filtered to remove the precipitated insoluble gel (crosslinked product). The filtrate was washed with water and evaporated to remove the solvent and unreacted comonomer and then stripped with steam at  $230\text{--}250^\circ\text{C}$  to remove the oily oligomer. The polymer (resin) was recovered as residue.

### Measurements

$^1\text{H-NMR}$  spectra of the polymers were recorded with an AC-P300 spectrometer. Intrinsic viscosities of the polymers were determined by an Ubbelohde viscometer in toluene at  $25^\circ\text{C}$ . The resin color was estimated by the Gardner color scale in 50% toluene, whereas the resin softening point was measured by the ring-and-ball method.

## RESULTS AND DISCUSSION

The result of PD polymerizations at various content of CPD ranging from 0 to 40% are given in Table I. All the copolymerizations give complete conversions, indicating high reactivities of comonomer in these copolymerization systems. The data of the intrinsic viscosities of the polymer given in Table I show that the polymer molecular weight remains nearly unchanged with the addition of CPD. By contrast, the softening point of the polymer is considerably increased by adding CPD in the polymerization, as shown in Figure 1. As the polymer bearing cyclic structures usually appears at a higher softening point than the corresponding linear polymer,<sup>1</sup> we conclude that the addition of CPD in the present PD polymerization

system does not exert an effect on the polymer molecular weight, but can raise the softening point of the polymer owing to the introduction of cyclic structures.

Table I shows that the Gardner color scale of the polymer gradually increases with the concentration of CPD. It must be said that the coloration mechanism of aliphatic petroleum resins is not yet very clear, but it is generally thought that unsaturated structures, particularly double bond-containing cycles, are mainly responsible for the color of this kind of polymer.<sup>1</sup> We conclude, therefore, that the augmentation of the content of unsaturated rings of CPD enchainments in the copolymer chain gives rise to darker polymer colors.

We have shown in previous articles that the cationic polymerization of PD is usually accompanied by the formation of insoluble gels (crosslinked polymers)<sup>5</sup> but the crosslinking reaction could be reduced or eliminated by aromatic compounds.<sup>6</sup> In our present polymerization system carried out in toluene, the homopolymerization of PD does not produce any crosslinked products. However, the result shown in Figure 2 indicates that with higher CPD proportions ( $>10\%$ ) the copolymerization generates insoluble crosslinked products as well as soluble polymers. It has been known that the crosslinking reaction of diene polymers always occurs on the residual double bonds contained in the polymer chain through protonation or cationization of the double bond,<sup>7</sup> hence we propose that the cyclic double bond carried by CPD structural units shows a higher reactivity toward carbocations than that contained in PD units. This result is in full accordance with the previously reported high reactivity of CPD resulting in gels.<sup>3</sup> The result that CPD leads easily to crosslinking demonstrates that the modification of the present PD polymerization by adding CPD is limited in a small range of CPD content.

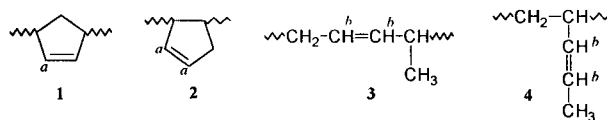


Figure 3 gives  $^1\text{H-NMR}$  spectra of the polymers. We fail to obtain any helpful information from the highly overlapped signals in the saturated region. In contrast, we observe clearly two separate peaks at 5.65 ppm (peak *a*) and 5.31 ppm (peak *b*), which are attributed to protons on double bonds carried by CPD enchainments (**1** and **2**)<sup>4</sup> and PD

**Table I** Copolymerizations of PD with CPD Initiated by  $\text{AlCl}_3$  in Toluene at  $40^\circ\text{C}$ 

No.	Comonomer composition		Yield <sup>a</sup> (%)	Color <sup>b</sup> (Gardner)	$ \eta $ <sup>b</sup> (dL/g)	CPD (%) in Polymer <sup>c</sup>
	PD (mol %)	CPD (mol %)				
1	100	0	~100	4	0.260	—
2	95	5	~100	5.5	0.275	5.0
3	90	10	~100	7	0.265	10.2
4	85	15	~100	8.5	0.258	14.5
5	80	20	~100	9	0.281	20.1

[PD + CPD] = 6.0 mol/L;  $[\text{AlCl}_3]$  = 0.045 mol/L; reaction time: 1.5 h.

<sup>b</sup> Comprising the polymer, oligomer, and crosslinked product.

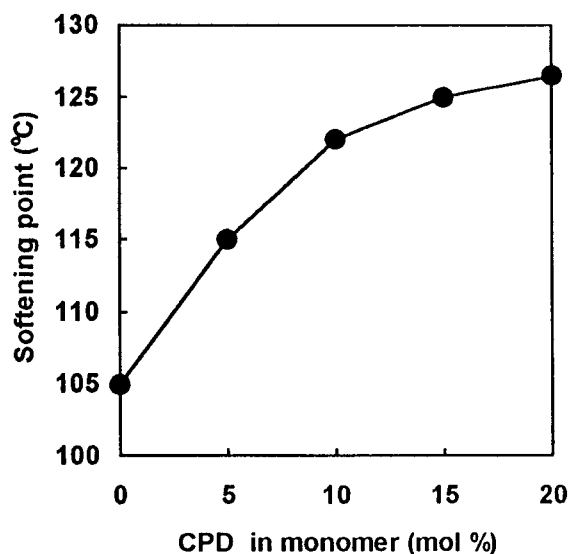
<sup>c</sup> Only for polymer (resin).

<sup>d</sup> Determined by  $^1\text{H-NMR}$  with eq. (1), see text.

segments (3 and 4),<sup>5</sup> respectively. Obviously, the proportion of CPD units in the copolymer chain can be calculated with integral intensities of peaks *a* and *b* (denoted *A* and *B*, respectively) according to the following equation:

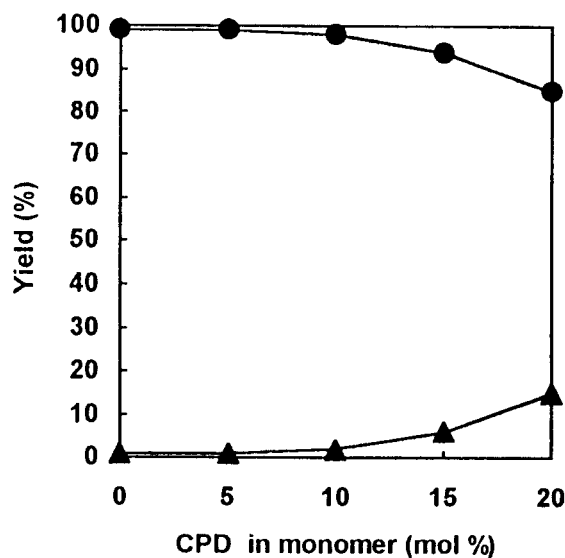
$$\text{CPD}(\%) = \frac{A}{(A + B)} \times 100\% \quad (1)$$

The CPD(%) values calculated by eq. (1) are given in Table I. These data give a perfect correlation with the starting comonomer compositions. Thus, the copolymer composition can be determined by  $^1\text{H-NMR}$  and calculated with ease by eq. (1).

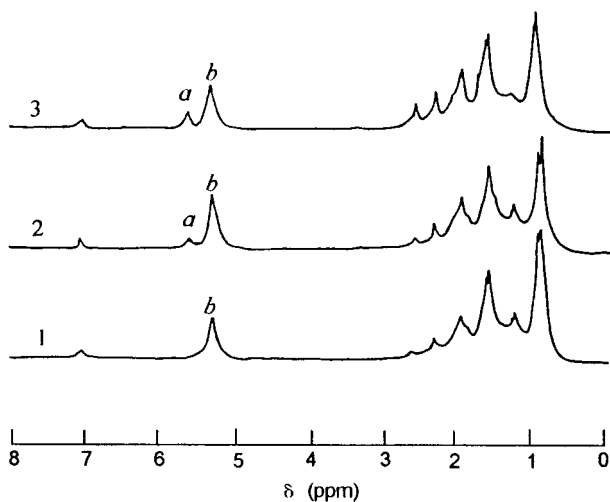


**Figure 1** Dependence of the polymer softening point on the proportion of CPD in comonomer. Reaction conditions given in Table I.

The fact that the high concentration of CPD results in crosslinking prevents us from determining two reactivity ratios of this copolymerization system by conventional methods. However, a series of low-conversion experiments at small CPD proportions permit calculating one single reactivity ratio according to the method proposed by Jaacks.<sup>8</sup> In the present copolymerizations of PD ( $M_1$ ) and CPD ( $M_2$ ) performed with rather low  $M_2$  concentrations, a large excess of  $M_1$  permits neglecting, in a first approximation, the monomer consumption by propagation of the carbocation  $\sim M_2^\oplus$ . With this simplification the two rate equations for  $M_1$  and  $M_2$  consumptions by their addi-



**Figure 2** Effect of the comonomer composition on yields of soluble polymer (●) and crosslinked polymer (▲). Reaction conditions given in Table I.



**Figure 3**  $^1\text{H-NMR}$  spectra of polymers prepared under reaction conditions shown in Table I. CPD proportion in comonomer: 0 (1), 10% (2), 20% (3).

tions to  $\sim M_1^\oplus$  can be expressed by the following equations:

$$-\frac{d[M_1]}{dt} = k_{11}[\sim M_1^\oplus][M_1] \quad (2)$$

$$-\frac{d[M_2]}{dt} = k_{12}[\sim M_1^\oplus][M_2] \quad (3)$$

By division we obtain

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}}{k_{12}} \cdot \frac{[M_1]}{[M_2]} = r_1 \cdot \frac{[M_1]}{[M_2]} \quad (4)$$

or

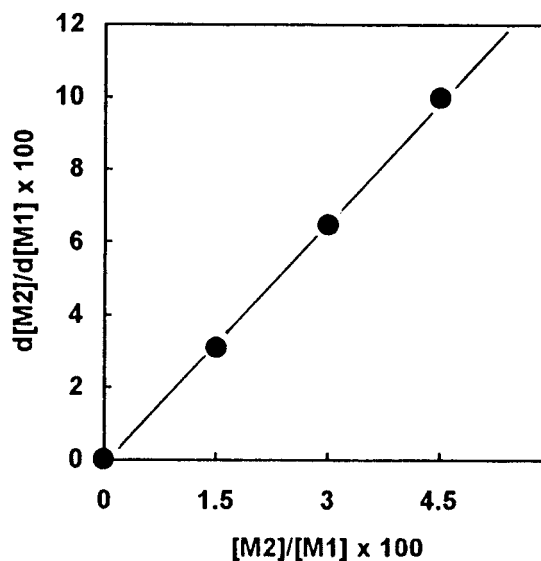
$$\frac{d[M_2]}{d[M_1]} = \frac{1}{r_1} \cdot \frac{[M_2]}{[M_1]} \quad (5)$$

Equation (5) reveals that a linear relationship exists between  $d[M_2]/d[M_1]$  and  $[M_2]/[M_1]$ . The  $d[M_2]/d[M_1]$  data could be obtained from the copolymer composition determined with  $^1\text{H-NMR}$  spectra according to eq. (1) while the  $[M_2]/[M_1]$  values could be directly obtained from the comonomer composition. Figure 4 shows the  $d[M_2]/d[M_1] - [M_2]/[M_1]$  plot for the low-conversion copolymerizations at low concentrations of CPD. From the reciprocal slope of the straight line we obtain  $r_1 = k_{11}/k_{12} = 0.46$ . This reactivity ratio value shows that CPD has a higher reactivity than PD toward PD growing carbocations, and

hence the copolymer has a higher CPD proportion than the corresponding comonomer.

## CONCLUSION

The cationic copolymerization of PD with CPD shows that the PD polymerization system induced by aluminium trichloride in toluene is strongly influenced by adding CPD. The following conclusions could be obtained by this work: (1) the softening point of the polymer is greatly raised by the introduction of cyclic structures of CPD, but the polymer molecular weight remained nearly constant; (2) the color scale of the polymer is increased with the addition of CPD due to the introduction of unsaturated rings; (3) at high CPD proportions in comonomer, the copolymerization produces insoluble gel as well as soluble polymer. That is, the modification of the polymerization of PD through introduction of CPD is limited in a small range of CPD concentration; (4) the reactivity ratio for the present PD( $M_1$ )-CPD( $M_2$ ) copolymerization determined by the Jaacks method is  $r_1 = 0.46$ . This value indicates that CPD has a higher reactivity than PD toward PD growing carbocations, and hence the copolymer has a higher CPC proportion than the starting comonomer.



**Figure 4** Determination of reactivity ratio  $r_1$ . Reaction conditions:  $[\text{PD} + \text{CPD}] = 5.0 \text{ mol/L}$ ;  $[\text{AlCl}_3] = 0.025 \text{ mol/L}$ ; solvent: toluene; reaction temperature:  $20^\circ\text{C}$ ; reaction time: 0.5 min; conversions:  $< 10\%$ .

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