

# Cationic Copolymerization of 1,3-Pentadiene with *endo*-Dicyclopentadiene

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Received 20 February; accepted 25 October 1996

**ABSTRACT:** Copolymerizations of 1,3-pentadiene (PD) with *endo*-dicyclopentadiene (DCPD) initiated by aluminum trichloride were carried out in toluene. The addition of DCPD in the PD polymerization system does not affect the molecular weight but increases greatly the softening point of the polymer due to the introduction of cyclic structures. The Gardner color scale of the polymer is also raised by the introduction of unsaturated rings of DCPD. The copolymerization gives complete conversions but generates insoluble crosslinked gels at high DCPD contents due to a higher crosslinking reactivity of DCPD than PD. The low-conversion experiments were carried out with small amounts of DCPD in order to determine the reactivity ratio in this copolymerization system ( $M_1 = \text{PD}$  and  $M_2 = \text{DCPD}$ ). The result of  $r_1 = k_{11}/k_{12} = 4.5$  demonstrates that DCPD has a lower reactivity than PD toward PD-growing carbocations, and hence, the copolymer shows a smaller DCPD proportion than the corresponding comonomer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1719–1723, 1997

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

## INTRODUCTION

The cationic polymerization of  $C_5$  fraction comprising a variety of  $C_5$  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 in determining the structure and property of the polymer.<sup>2</sup> For example, the content of cyclic  $C_5$  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 linear polymer chain.<sup>1</sup> We recently became interested in the copolymerization of 1,3-pentadiene (PD) and *endo*-dicyclopentadiene (DCPD, the dimer of 1,3-cyclopentadiene), the most important linear and cy-

clenic dienes in the  $C_5$  fraction, respectively. It has been found that DCPD shows a moderate cationic polymerizability.<sup>3,4</sup> However, its cationic copolymerization with PD, which is of applicable significance, has never appeared in the current literature.

In this work, PD-DCPD copolymerizations were induced by  $AlCl_3$  in toluene. The investigations concern 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.

## EXPERIMENTAL

### Materials

Commercial PD from Fluka with a purity of 90% was dried with  $CaH_2$  and distilled. DCPD from Aldrich with a purity of 95% was distilled over  $CaH_2$  under reduced pressure. The solvents were

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**Table I** Copolymerizations of PD with DCPD Initiated by AlCl<sub>3</sub> in Toluene at 40°C<sup>a</sup>

| No. | Comonomer Composition |              | Yield <sup>b</sup> (%) | Color <sup>c</sup> (Gardner) | [η] <sup>c</sup> (dL/g) |
|-----|-----------------------|--------------|------------------------|------------------------------|-------------------------|
|     | PD (mol %)            | DCPD (mol %) |                        |                              |                         |
| 1   | 100                   | 0            | ~ 100                  | 4                            | 5.25 × 10 <sup>-2</sup> |
| 2   | 90                    | 10           | ~ 100                  | 5                            | 5.23 × 10 <sup>-2</sup> |
| 3   | 80                    | 20           | ~ 100                  | 5.5                          | 5.36 × 10 <sup>-2</sup> |
| 4   | 70                    | 30           | ~ 100                  | 6                            | 5.98 × 10 <sup>-2</sup> |
| 5   | 60                    | 40           | ~ 100                  | 6.5                          | 5.23 × 10 <sup>-2</sup> |

<sup>a</sup> [PD + DCPD] = 5.0 mol/L; [AlCl<sub>3</sub>] = 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).

also distilled over CaH<sub>2</sub>. AlCl<sub>3</sub> was purified by sublimation in vacuum.

### Polymerization

The polymerizations were carried out in a three-necked reactor in dry nitrogen atmosphere. The solvent was introduced in the reactor first, and then the initiator was added. 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 under reduced pressure to remove the solvent and unreacted comonomer. It was then stripped with steam at 230–250°C to remove the oily oligomer. The polymer (resin) was recovered as a residue.

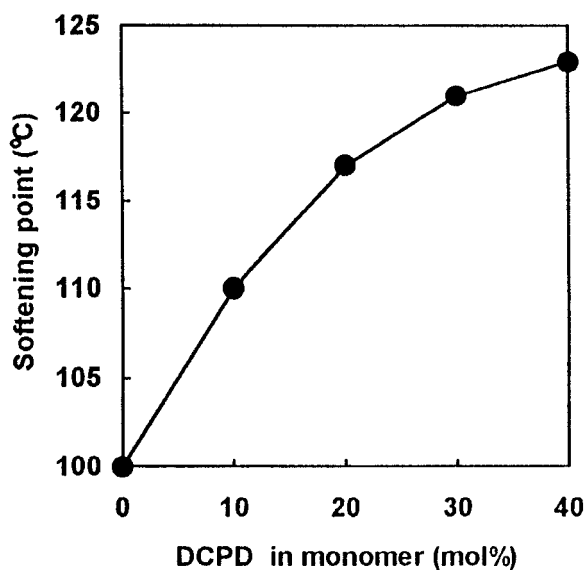
### Measurements

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra of the polymers were recorded with a AC-P300 spectrometer. The intrinsic viscosities of the polymers were determined with an Ubbelohde viscometer in toluene at 25°C. The resin color was estimated by use of the Gardner color scale in 50% toluene, whereas the resin-softening point was measured by use of the ring and ball method.

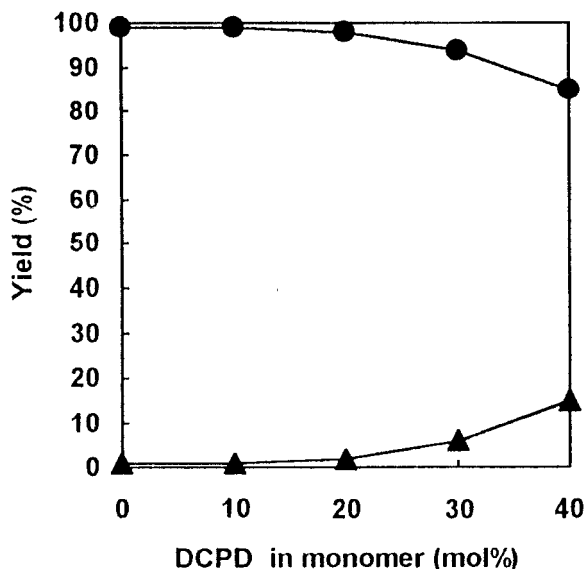
## RESULTS AND DISCUSSION

The results of PD polymerizations at various contents of DCPD ranging from 0 to 40% are given in Table I. All of these copolymerizations give complete conversions, indicating high reactivities

of the 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 DCPD. By contrast, the softening point of the polymer is considerably increased by adding DCPD in the polymerization, as shown in Figure 1. Because the polymer bearing cyclic structures usually appear to have a higher softening point than the corresponding linear polymer,<sup>1</sup> we conclude that the addition of DCPD 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.



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



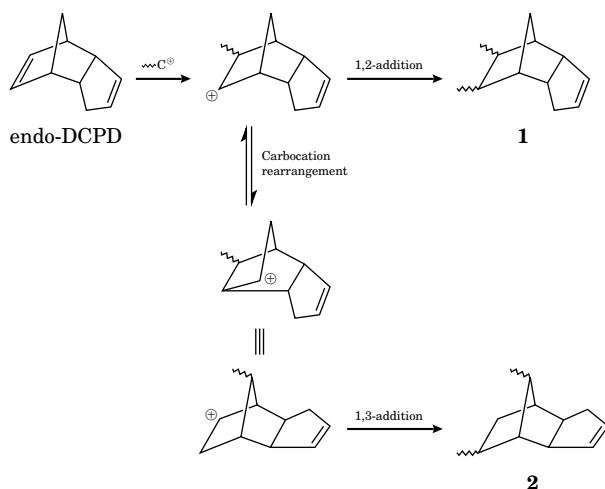
**Figure 2** Effect of the comonomer composition on yields of (●) soluble polymer and crosslinked polymer (▲). Reaction conditions are given in Table I.

Table I also shows that the Gardner color scale of the polymer gradually increases with the concentration of DCPD. 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 DCPD enchainments in the copolymer chain gives rise to darker polymer colors.

We have shown in previous works that the cationic polymerization of PD is usually accompanied by the formation of insoluble gels (crosslinked polymers)<sup>5</sup> but that the crosslinking reaction could be reduced or eliminated by aromatic compounds.<sup>6</sup> In this 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 DCPD proportions (more than 30%), the copolymerization generates insoluble crosslinked products as well as soluble polymers. It is 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 DCPD structural units shows a higher reactivity

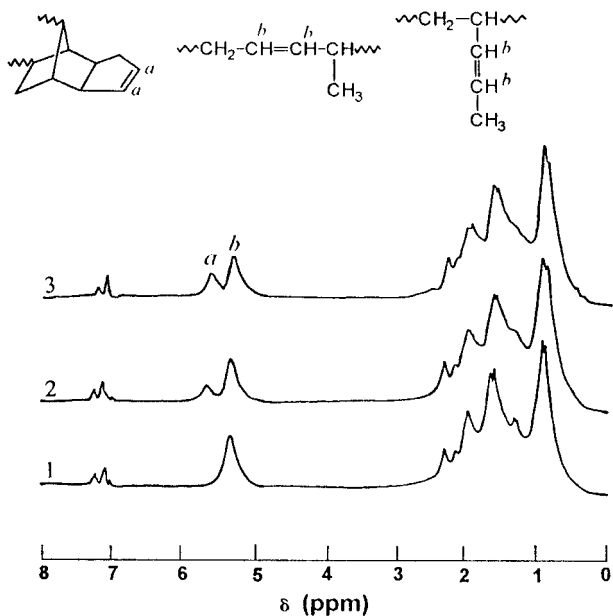
toward carbocations than that contained in PD units. The result that DCPD leads easily to crosslinking demonstrates that the modification of the present PD polymerization by adding DCPD is limited in a range of DCPD content.

In order to get insight into the microstructure of the copolymer chains, we obtained <sup>1</sup>H NMR spectra of the polymers shown in Figure 3. We failed to obtain any helpful information from the highly overlapped signals in the saturated region except two strong signals at 0.95 and 1.60 ppm, attributed to the 1,4- and 1,2-addition PD segments.<sup>5</sup> In contrast, we clearly observe two separate peaks at 5.63 (peak *a*) and 5.31 (peak *b*) ppm, arising from DCPD and PD enchainments, respectively. As to the cationic polymerization of DCPD bearing two double bonds (norbornenic and cyclopentenic double bonds), the addition occurs through the more active norbornenic double bond.<sup>4</sup> According to Corner et al.,<sup>3</sup> two kinds of structural units can be generated through two paths, illustrated by the following scheme:



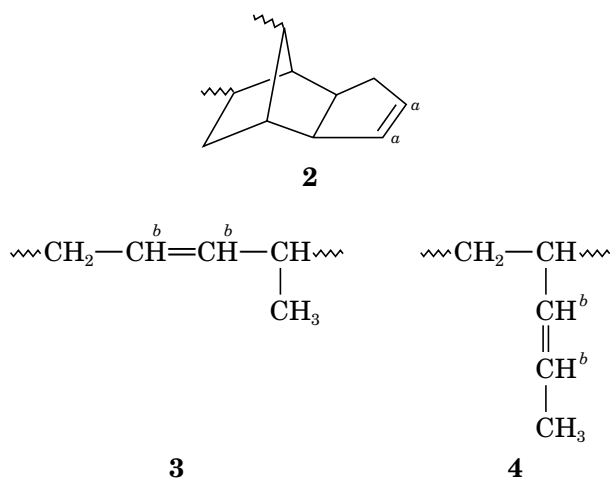
As shown above, the cationized DCPD can pursue a direct 1,2-addition to give the endo-DCPD unit (1) or undergo a carbocation rearrangement and then a 1,3-addition to generate the exo-unit (2). Because structural units 1 and 2 show two <sup>1</sup>H NMR signals at 5.40 and 5.65 ppm, respectively,<sup>3</sup> we suggest that the PD-DCPD copolymer prepared under our conditions contains only structural unit 2, which gives the peak *a* at 5.63 ppm on the spectra in Figure 3.

This structural consideration is fully supported by the evidence from the IR spectra shown in Figure 4. The copolymer shows two absorptions, characteristic of the DCPD segment at 700 and 740  $\text{cm}^{-1}$ . The shape of these two peaks strongly con-



**Figure 3**  $^1\text{H}$  NMR spectra of polymers prepared under the reaction conditions shown in Table I. DCPD proportion in comonomer: (1) 0, (2) 20%, (3) 40%.

firmly the presence of the exo-unit 2, that is, the peak at  $700\text{ cm}^{-1}$  appears much stronger than that at  $740\text{ cm}^{-1}$ .<sup>3</sup> Unit 1, giving a strong band at  $740\text{ cm}^{-1}$  and a weak peak at  $700\text{ cm}^{-1}$ , seems absent or at least negligible. Therefore, the above results obtained from the polymer spectra indicate that copolymer chains consist mainly of exo-DCPD enchainments (2) and 1,4-addition and 1,2-addition PD segments (3 and 4, respectively)



The fact that the high concentration of DCPD results in crosslinking prevents us from determining two reactivity ratios of this copolymerization system by conventional methods. However, a se-

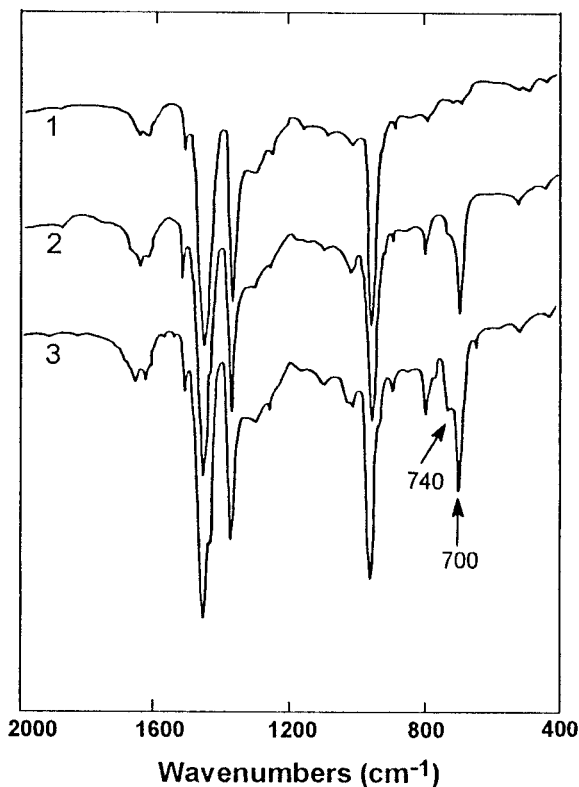
ries of low-conversion experiments at small DCPD proportions permit us to calculate one single reactivity ratio according to the method proposed by Jaacks.<sup>8</sup> In fact, the experiments were carried out with a DCPD proportion in the comonomer of less than 10%, so that the formation of gels could be avoided.

In these copolymerizations of PD ( $M_1$ ) and DCPD ( $M_2$ ), performed with rather low  $M_2$  concentrations, a large excess of  $M_1$  permits us to neglect in a first approximation the monomer consumption by the propagation of the carbocation  $\sim M_2^\oplus$ . With this simplification, the two rate equations for  $M_1$  and  $M_2$  consumptions by their additions to  $\sim M_1^\oplus$  can be expressed by the following equations:

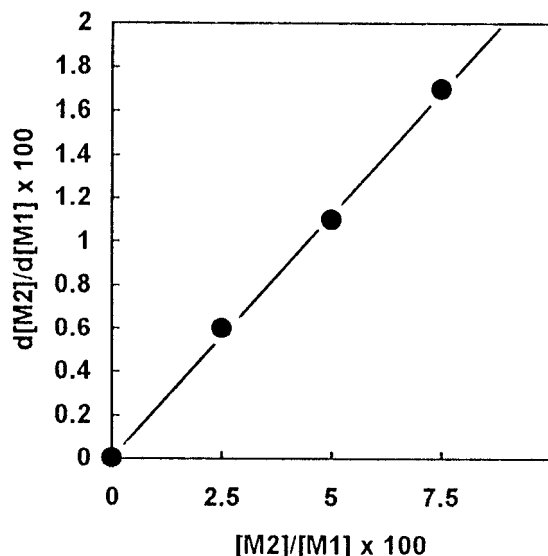
$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\oplus][M_1] \quad (1)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^\oplus][M_2] \quad (2)$$

By division, we obtain:



**Figure 4** IR spectra of polymers prepared under the reaction conditions shown in Table I. DCPD proportion in comonomer: (1) 0, (2) 20%, (3) 40%.



**Figure 5** Determination of reactivity ratio  $r_1$ . Reaction conditions: [PD + DCPD] = 5.0 mol/L; [AlCl<sub>3</sub>] = 0.025 mol/L; solvent = toluene; reaction temperature = 20°C; reaction time = 0.5 min; conversions = <10%.

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}}{k_{12}} \cdot \frac{[M_1]}{[M_2]} = r_1 \cdot \frac{[M_1]}{[M_2]} \quad (3)$$

or

$$\frac{d[M_2]}{d[M_1]} = \frac{1}{r_1} \cdot \frac{[M_2]}{[M_1]} \quad (4)$$

Eq. (4) 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 IR spectra with the peak at 700 cm<sup>-1</sup>, while the  $[M_2]/[M_1]$  values could be directly obtained from the comonomer composition. Figure 5 shows the  $d[M_2]/d[M_1]$  –  $[M_2]/[M_1]$  plot for the low-conversion copolymerizations at low concentrations of DCPD. From the reciprocal slope of the straight line, we obtain:  $r_1 = k_{11}/k_{12} = 4.5$ . This reactivity ratio value shows that DCPD has a lower reactivity than PD toward PD-growing carbocations, and hence, the copolymer has a lower DCPD proportion than the corresponding comonomer.

## CONCLUSION

The cationic copolymerization of PD with DCPD shows that the PD polymerization system induced by aluminum trichloride in toluene is strongly influenced by the addition of DCPD. The following conclusions could be drawn by this work:

- 1) The softening point of the polymer is greatly raised by the introduction of cyclic structures of DCPD, but the polymer molecular weight remained nearly constant.
- 2) The color scale of the polymer is slightly increased with the addition of DCPD due to the introduction of unsaturated rings.
- 3) At high DCPD proportions in the comonomer, the copolymerization produces insoluble gel as well as soluble polymer. That is, the modification of the polymerization of PD through the introduction of DCPD is limited in a range of DCPD concentrations.
- 4) The reactivity ratio for the present PD( $M_1$ )-DCPD( $M_2$ ) copolymerization determined by Jaacks' method is:  $r_1 = 4.5$ . This value indicates that DCPD has a lower reactivity than PD toward PD-growing carbocations, and hence, the copolymer has a smaller DCPD proportion than that of the starting comonomer.

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