Polymerization of Dicyclopentadiene: A New Reaction Injection Molding System

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Synopsis

Dicyclopentadiene was polymerized by reaction injection molding (RIM) using a catalyst system based on WCl_6 and diethylaluminium chloride. Ring opening polymerization results in formation of a crosslinked polymer with a high crosslink density. The kinetics of the fast exothermic reaction was followed by the adiabatic temperature rise method. In addition to the "adiabatic" polymerization, isothermal reactions were carried out in a thin mold. The properties of the cured samples were determined by dynamic mechanical measurements, sol-gel analysis, gas chromatography, mass spectrometry, DSC, and IR spectrometry. Gel fraction, glass transition temperature, content of the unreacted monomer, the modulus, and the degree of swelling were used to characterize the cured samples. The system shows very low critical conversion at the gel point ($a_c < 0.01$) proving a chainwise mechanism of the polymerization. Possible participation of a cationic mechanism is discussed. We found the specific reaction temperature range ($T = 100-140°C$) for optimum properties of the cured samples. Deterioration of properties (decrease in the crosslinking density, etc.) at a high temperature is a result of a faster deactivation of catalytic centers and a reversibility of the exothermic ring opening polymerization. Reverse cyclodegradation is preferred at a higher temperature.

INTRODUCTION

Cyclic olefins can be polymerized using Ziegler–Natta type catalysts by ring-opening mechanism.[1] A wide variety of catalysts were mentioned that initiate the polymerization of cycloolefins. However, the most efficient proved to be a combination of tungsten or molybdenum compounds and alkylaluminium chlorides. Scott et al.[2] revealed that the mechanism of the ring opening polymerization of cycloolefins is the same as that of metathesis of acyclic olefins resulting in transalkylidenation. It is supposed[3] that a catalytically active center consists of the carbene of a transition metal, Me. Polymerization proceeds by an insertion of the monomer cycloolefin unit into the active Me = alkyl bond leading to the formation of polymers with an unsaturated backbone. The course of the reaction, the yield and the structure of the resulting polymer strongly depend on the composition of the catalyst.[4]

Ring opening polymerization is an exothermic, very fast reaction even at a low temperature. Reaction is initiated instantaneously by adding the catalyst, and no heating is necessary. These properties make the ring opening polymerization of cycloolefins a suitable system for application in RIM processing. The main requirements for a reaction system to be RIM processable were summarized by Macosko[5]: fluid reactants of an appropriate

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viscosity allowing good mixing, fast reaction with cure times less than 3 min, curing without byproducts, and a solidification in a mold by cross-linking or phase separation.

All these requirements are met in the new RIM system based on the ring opening polymerization recently developed by Hercules Inc. A bifunctional monomer, dicyclopentadiene (DCP), was used to form a highly crosslinked polymer. Geer has already reported[6] on the polymerization of DCP and revealed the excellent properties of the resulting thermoset. The DCP is cured at a slightly increased temperature within a few seconds using the catalyst developed at Hercules Research Center.[7] The extremely fast reaction can be retarded by an inhibitor to enable a mold to be filled.

In this paper we attempt to explain the course and the reaction mechanism of DCP polymerization under the conditions of RIM processing. A scheme of the reaction is given in Figure 1.

EXPERIMENTAL

Chemicals and composition of the reaction mixture. Monomers, endo-dicyclopentadiene (DCP), and norbornene (NOR), as well as the catalyst system, were used as obtained from Hercules Inc. Purity of DCP was about 99%, and all chemicals were kept at room temperature under nitrogen. The two-part metathesis catalyst system developed in Hercules Research Center[7] consists of the catalyst—modified WCl_6—and the cocatalyst—di-ethylaluminium chloride. Modification of WCl_6 with phenol and acetyla-cetone was described elsewhere.[7] Di-n-butyl ether was used as an inhibitor.
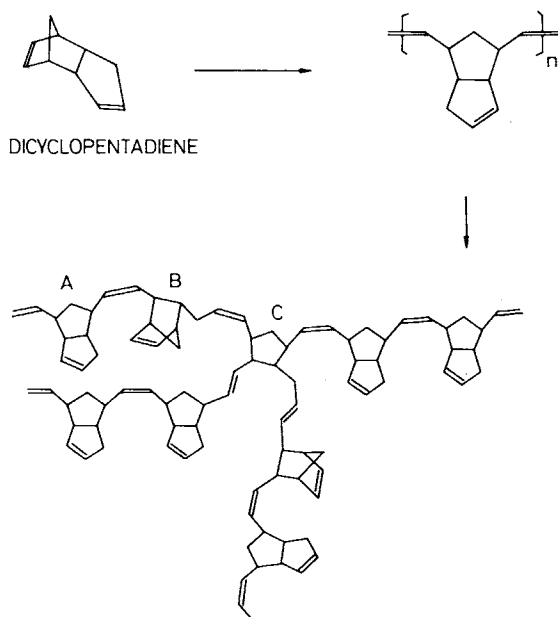

Fig. 1. Scheme of DCP polymerization and the resulting poly DCP structure: (unit A) polymerization through the norbornene ring; (unit B) polymerization through the cyclopentene ring; (unit C) crosslink or branch.

Molar composition of the reaction mixture for the DCP polymerization was the following: DCP:catalyst:cocatalyst = 2000:1:7. In addition, the mixture contained 3 wt % toluene and a variable content of the inhibitor. Norbornene (NOR) was polymerized in a 20 wt % chlorobenzene solution. The composition of the reaction mixture was as follows: NOR:catalyst:cocatalyst = 1000:1:6.

Experimental Technique. Reaction injection molding (RIM) was used to polymerize DCP by mixing the two reaction components: component A—DCP and catalyst—and component B—DCP, cocatalyst and inhibitor. The samples were prepared using the mini-RIM (a small version of the industry standard machine) and a small manual RIM machine of the University of Minnesota. In the manual machine, two syringes for the components A and B were mounted in a lever arm device and connected to the mixhead by tubing. The RIM machines were modified to maintain the anaerobic conditions using a dioctyl phthalate oil reservoir behind the cylinders, rubber septums on the tanks for monomers, and dry nitrogen inlets. Reaction components A and B were anaerobically transferred into the RIM machine, and the machine together with the reaction vessel were purged with dry nitrogen.

Different polymerization vessels were used: (a) polypropylene cup thermally insulated with vermiculite: (b) silicone Tygon tube without any thermal insulation; and (c) stainless steel mold. The thermocouples were placed in the reaction vessel.

The thermally insulated cup represents an adiabatic reaction medium. The silicone hose and the steel mold with a large noninsulated surfaces were used for the study of the nonadiabatic course of the reaction. The geometric position of the thermocouple in the sample was also used to study different thermal conditions.

A series of samples with a variable content of inhibitor were polymerized in different reaction vessels and with different position of the thermocouple in the sample. Specification of the samples and the abbreviation used in the paper are the following:

Cup 1: sample prepared in the cup with 1% inhibitor.

Cup 2: 3% inhibitor—cup center or surface—the thermocouple was placed in the center or at the surface of the sample; for the analysis, the sample was cut from the center or the surface of the original polymerized sample.

Cup 3: 10% inhibitor.

Mold: sample prepared in a mold with 3% inhibitor—mold runner or vent; the thermocouple was placed in an inner part close to the runner of the mold or at the far end of the plaque (vent); for the analysis, the sample was cut from the plaque close to the runner or to the vent, respectively.

Hose: the sample was prepared in the silicone hose with 10% inhibitor.

Plaques 2 mm and 0.2 mm thick were prepared from the molds.

Polymerization of norbornene was carried out in a dry box under nitrogen.

Analysis. The course of the reaction was followed by the adiabatic temperature rise method (ATR) using a computer-controlled data acquisition system. This system uses an off-board A/D converter to translate the analog thermocouple signal to a string of digital data. Temperature was recorded every 0.1 s with an accuracy of 0.5°C.

For the kinetic study in a pregel stage, the reaction was quenched at different reaction times with an excess of butanol and the sample was analyzed by gas chromatography. The critical conversion was eluated by the interpolation of a conversion–time curve to the time of gel formation determined visually.

The Hewlett Packard 5840A gas chromatograph with a flame ionization detector was used. The oven temperature was 140°C, and the carrier gas was nitrogen. Cumene was used as an internal standard for calibration.

Mass spectra were measured with the in line system GCMS Finnigan 4000 at the oven temperature 100°C and with the energy 70 eV. The thermal properties of cured samples were determined using a DSC apparatus Mettler TA 3000, programmed at a heating rate of 10°C/min. DSC was purged with dry nitrogen. IR spectra of thin sample films were measured using the Perkin-Elmer 580 B spectrometer in the range from 4000 to 600 cm^{-1}.

Mechanical properties of the samples were measured with the Rheometrics System Four. Thick plaques (thickness 2 mm, length 40 mm, width 10 mm) were measured in torsion using a dynamic experiment. The dependence of the storage modulus G', loss modulus G'', and tan δ on the temperature was followed at the strain 0.1% and the strain rate 1 rad/s. The equilibrium modulus G_e was determined by static stress relaxation in torsion. The time dependence of the modulus $G(t)$ was followed at 225°C and extrapolated to equilibrium. Thin sample films (0.2 mm, 40 mm, 5 mm) were measured in slight tension by dynamic measurement with the rate 1 rad/s and an automatic adjustment of strain, starting from 0.1%.

RESULTS

The ring opening polymerization of DCP is an exothermic reaction due to release of the strain energy of the ring. Hence, the polymerization kinetics was followed by a temperature rise during the reaction using the adiabatic method (ATR). For a simple reaction mechanism, the conversion during an irreversible reaction is proportional to the evolved heat and, under adiabatic conditions, to the temperature rise. These criteria are not met in our case, so that the conversion was not evaluated from the ATR plots. Nevertheless, the ATR gives at least qualitative information about the reaction kinetics.

"Adiabatic" Polymerization

Figure 2 shows the reaction course of several systems under study. Description and indication of the samples is given in the experimental part. The systems differ in content of the inhibitor and in the thermal conditions determining the heat loss during the reaction. Heat loss depends on the type of reaction vessel (cup, hose, mold), its thermal insulation, and the thermocouple position in the vessel.

The reaction is very fast and after an induction period, the temperature increases by 190°C within a few seconds. In general, the course of the reaction shows four typical stages: (1) induction period; (2) first exotherm, (3) second exotherm; (4) small endotherm at 180°C.

The important characteristic of a system is the maximum temperature during the reaction (T_{max}) depending on the thermal insulation of the sys-
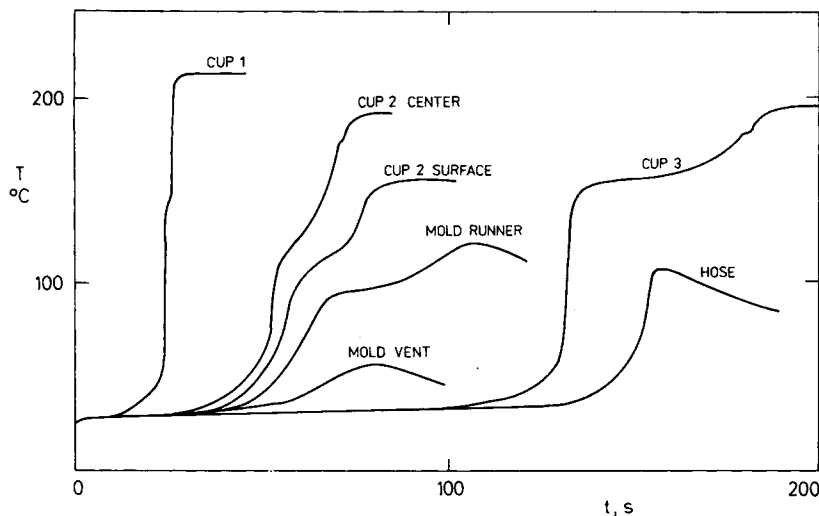
Fig. 2. Dependence of the reaction mixture temperature on the reaction time during DCP polymerization (for the abbreviation see the experimental part): (cup 1) 1% inhibitor; (cup 2, mold) 3% inhibitor; (cup 3, hose) 10% inhibitor.

tem. Figure 2 and Table I show that a larger heat loss at the surface of the sample (cup surface) results in a lower T_{max} compared to the center of the sample (cup center). Also, T_{max} is lower in the vent than in the runner of a mold. In cases where heat loss is large enough, the second exotherm does not appear.

We have found that a gel is formed in the early stage of the reaction during the induction period. The critical conversion at the gel point (α_c) is less than 1%. Dilution of the reaction mixture with dry toluene shifts the critical conversion to a somewhat higher value. For samples with the toluene content 0%, 10%, and 20 vol%, resp., the critical conversions are: α_c

TABLE I
Properties and Structural Parameters of PolyDCP Samples Prepared by the RIM Technique ("Adiabatic" Polymerization)[a]

Sample[b]	T_{max} (°C)	$G' \times 10^7$ (Pa)	$G_e \times 10^7$ (Pa)	T_g (°C)	w_g	q
Cup 1	213	0.72	0.6	119	1.0	1.47
Mold runner	120	4.0	2.9	50	0.987	1.25
Mold runner—2nd run		5.0	5[c]	79	0.993	1.18
Mold vent	56	2.7		50	0.982	1.47
Cup 3	195	0.97		42	0.96	1.38
Hose	110	1.0[d]		53	1.0	1.28
Cup 2 center	194				0.97	1.35
Cup 2 surface	155				0.998	1.27

[a] T_{max} = the maximum temperature during the reaction, G' = shear storage modulus, G_e = shear equilirium modulus, T_g = temperature of glass transition, w_g = weight fraction of the gel, q = volume degree of swelling. The moduli were measured at temperatures $T = 250$°C (G') and $T = 225$°C (G_e), respectively.

[b] For the abbreviations of samples, see Experimental.

[c] $T = 229$°C.

[d] $T = 220$°C.

(0%) < 0.01, α_c (10%) = 0.010, α_c (20%) = 0.015. Length of the induction period depends on concentration of the inhibitor and only slightly on thermal conditions (Fig. 2). Dilution of a sample with toluene extends the induction period.

Beyond the gel point, the polymerization of DCP cannot be efficiently quenched with butanol because of the relatively slow diffusion into the gel. Consequently, another approach was used to study the polymerization. We evaluated and compared the final properties of reacted samples prepared under different conditions.

Mechanical Properties

We were mainly interested in values of the glass transition temperature T_g and the modulus of a sample in the rubbery state. Whereas the modulus gives information about the crosslink density of a network, T_g is affected both by the crosslink density, and by the content of a plasticizer (unreacted monomer, sol fraction). The temperature dependence of the storage modulus G', loss modulus G'', and tan δ of several systems is shown in Figure 3. In addition, the equilibrium modulus G_e was measured by stress–relaxation. Relatively good agreement was obtained between G' in the rubbery region from the dynamic experiments and the G_e value. T_g values were determined from the maximum of the temperature dependence of tan δ at the rate of the dynamic experiment 1 rad/s. Results are summarized in Table I.

Of a major importance is the fact that the sample cup 1 with the highest T_{max} shows the highest T_g but the lowest modulus (Table I). The sample
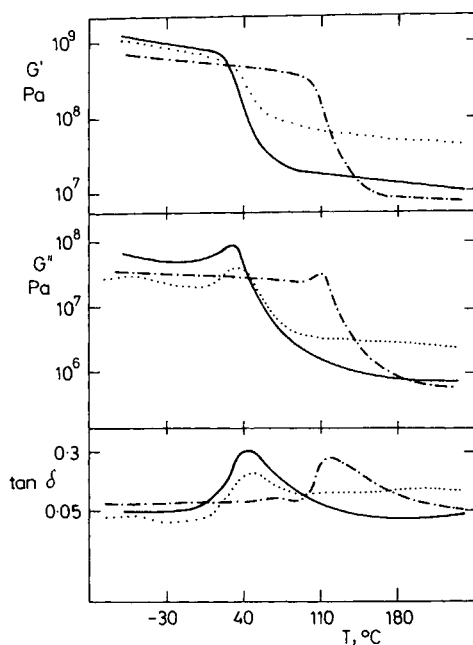

Fig. 3. Dependence of the storage modulus G', loss modulus G'', and tan δ of the polyDCP samples on temperature (for abbreviations see the experimental part): (—) cup 3; ($\cdots$) mold runner; (- · - ·) cup 1.

from a hose has both a higher T_g and modulus than that from cup 3, where a higher T_{max} was found. On the contrary, a higher modulus was observed in the runner than in the vent of a mold where lower T_{max} was found. Figure 4 shows the dependence of T_g on the T_{max}.

During the temperature sweep of a mechanical measurement in the Rheometrics System Four a sample was heated up to 250°C. Upon the repeated measurement of this sample higher values of T_g and the modulus were determined (Table I). This implies that the modulus and T_g increase by heating the cured sample.

Gel Fraction and the Degree of Swelling

The samples were extracted and swollen in toluene. The degree of swelling q and values of gel fraction w_g were determined, and the results are given in Table I. Volume degree of swelling is defined as

$$q = 1 + \frac{\rho_{pol}}{\rho_{tol}} \left(\frac{m_{sw}}{m_{dry}} - 1 \right)$$

where ρ_{pol} and ρ_{tol} are the density of the polyDCP and toluene, respectively, m_{sw} and m_{dry}, respectively, are the weight of the sample swollen in equilibrium in toluene and the weight of the dry sample.
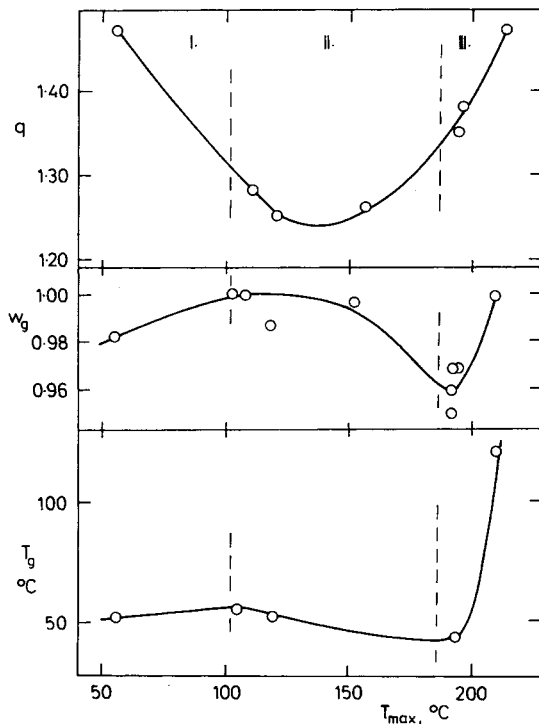

Fig. 4.   Dependence of the degree of swelling q, gel fraction w_g, and the glass transition temperature T_g of polyDCP samples on the maximum reaction temperature.

The crosslink density ν was calculated from the modulus in the rubbery state according to the expression $\nu = G'/RT$. Entanglements and the possible effect of a phantom behavior of the network were neglected in the calculation. Independent information about the relative crosslink density is obtained from the degree of swelling q, which is inversely proportional to ν (see Fig. 4).

The crosslink density of the most dense network—mold runner—calculated from the modulus is $7.0-9.2 \times 10^{-3}$ mol/cm³. The theoretical value $\nu_{th} = 15.2 \times 10^{-3}$ mol/cm³ ($\nu_{th} = 2/M_{DCP}$, where M_{DCP} is the molecular weight of the DCP unit. The number 2 stems from the fact that DCP is bifunctional and issues 2 elastically active chains).

The results (Fig. 4) reveal the dependence of the properties of cured samples on the maximum reaction temperature. A pronounced maximum was observed in the temperature range $T_{max} = 100-140°C$. However, T_{max} is not the only parameter in which the studied systems differ. Hence, independent proof was necessary to verify the hypothesis that the reaction temperature was affecting the sample properties.

Isothermal Polymerization

Unlike the "adiabatic" conditions, we arranged the experiment to assure the best possible heat transfer between the reaction mixture and the surroundings. The polymerization was carried out in a mold with a thickness of 0.2 mm preheated to a certain reaction temperature. The heat transfer from or to the sample is so fast in this case that one can assume isothermal conditions during the polymerization. The temperature of the reaction mixture is equal to that of a mold wall. The thin samples proved to be extremely sensitive to oxidation, and, in order to prevent oxidation, we analyzed them immediately after the polymerization.

Swelling and Extraction

The thin samples were extracted in toluene in the presence of the stabilizer, butyl hydroxytoluene, and the extracts were analyzed by gas chromatography and mass spectrometry. A low molecular weight compound corresponding to DCP indicated by the elution time of the gas chromatographs was found in the extracts. The mass spectra confirmed the presence of DCP in the extracts. The spectrum shows the molecular ion of DCP at $m/z = 132$, and the main splitting product cyclopentadiene at $m/z = 66$. Also, the remaining fragmentation corresponds to DCP as is obvious from Figure 5. The DCP content in the extracts of the samples was determined by gas chromatography, and its dependence on the reaction temperature is presented in Figure 6.

Thin samples undergo partial oxidation during swelling and subsequent drying procedure even in the presence of the stabilizer and drying in vacuum. The oxidation causes a decrease in sample permeability[8] and the entrapping of the solvent in the sample during the swelling–drying cycle. From Figure 6 it is obvious that samples prepared at high reaction temperature were more susceptible to oxidation which resulted in failure to remove all the solvent and in the apparent values $(w_g)_{app} > 1$.
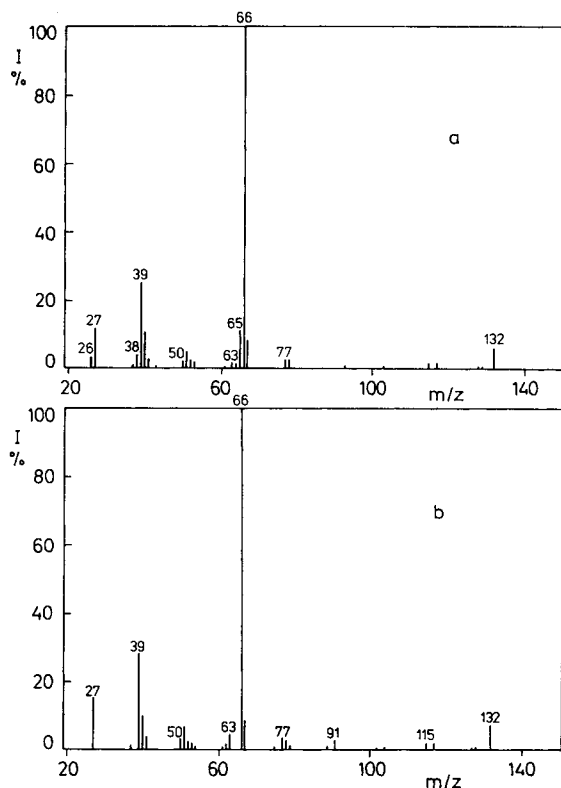
Fig. 5. Mass spectrum determined for the gas chromatography peak corresponding to DCP on the in line GC–MS apparatus: (a) extract of the polyDCP sample in toluene; (b) DCP.

Mechanical Properties

The dependence of the thin plaque tensile storage modulus E' and tan δ on temperature is shown in Figure 7. The values of T_g and E' in the rubbery region are summarized in Table II. Figure 7 presents the effect of the oxidation of samples: broadening of the glass transition and shifting the transition to a higher temperature. Enhancement of the modulus in the rubbery region due to the oxidation was also observed.

The dependence of properties and structural parameters on the reaction temperature in the isothermal polymerization (Fig. 6) shows the same maximum as in the case of the "adiabatic" experiments using T_{max}.

IR Spectroscopy and DSC

IR spectra of thin polyDCP samples prepared at temperatures from 25 to 210°C are presented in Figure 8. Assignment of the bands was summarized by Dall'Asta et al.[9] The figure shows an intense band at 1650 cm^{-1} assigned to the open chain *cis* double bond, formation of which is typical of the metathesis of cycloolefins. The bands at 1570 and 1620 cm^{-1} correspond to double bonds in the norbornene and cyclopentene rings, respectively. The ratio of absorption of these bands (1570/1620) decreases with increasing reaction temperature, indicating that the polymerization proceeds prefer-
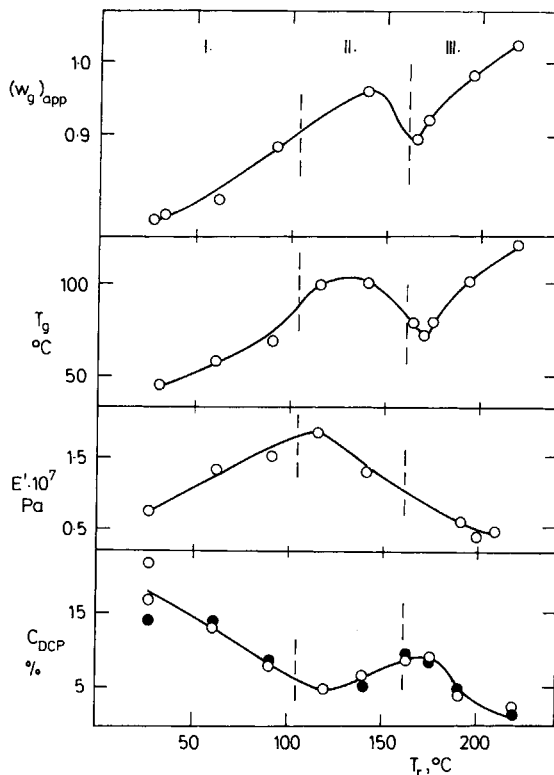
Fig. 6. Dependence of properties of thin polyDCP samples on reaction temperature (T_r) (isothermal polymerization). C_{DCP} = content of unreacted monomer in the polymer; $(w_g)_{app}$ = apparent value of w_g; (●) analysis in the Hercules Research Center.

ably through the norbornene ring of DCP. The figure also reveals an increase in the unassigned band at 1805 cm^{-1} with increasing reaction temperature.

DSC dynamic thermogram of the samples prepared at a low temperature shows three peaks in the temperature range 0–400°C: the endotherm at 210°C and the exotherms at 260 and 360°C (Fig. 9). A new exotherm at 150°C appears in the thermogram of the sample prepared at the high temperature ($T_{reaction}$ = 210°C). Likewise oxidation of the thin samples results in the appearance of the exotherm at 150°C (see Fig. 9). The thermograms were run in nitrogen atmosphere. Rescanning always leads to disappearance of the peaks in the temperature range up to the end-point temperature of the previous scan. The endotherm at 210°C and the exotherm at 360°C are accompanied by some weight loss, unlike the exotherm at 150°C. The heat capacity of the polyDCP ranges from 2.1 J/g deg in the glassy state of a highly crosslinked sample to 2.9 J/g deg in the rubbery state of a more loose polyDCP network.

Norbornene Polymerization

In addition to DCP, the polymerization of a model monofunctional monomer was also studied. The ring opening polymerization of norbornene was
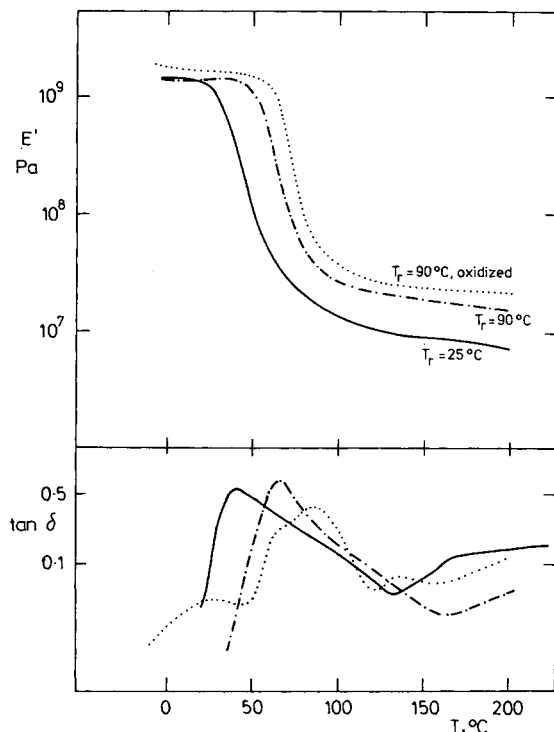
Fig. 7. Dependence of the tensile storage modulus E' and tan δ of thin polyDCP samples on temperature. The samples were prepared by isothermal polymerization at different reaction temperatures (T_r); (—) $T_r = 25°C$; (- - - -) $T_r = 90°C$; (· · ·) $T_r = 90°C$, oxidized sample.

carried out in chlorobenzene solution using the same catalyst system as in the case of DCP polymerization. Crosslinking occurs even in this case; the critical conversion at the gel point in the diluted system was found to be $\alpha_c = 0.02$.

TABLE II
Properties of Thin PolyDCP Samples Prepared by Isothermal Polymerization at T_r[a]

Reaction temp T_r (°C)	$E' \times 10^7$ (Pa)	C_{DCP} (%)	T_g (°C)
25	0.72	21.9	43
		16.7	
60	1.3	12.9	56
90	1.52	8.1	67
115	1.83		99
120		4.7	
140			99
165		8.6	78
175		9.6	78
195	0.6	4.1	
210	0.41		
220	0.44	2.4	125

[a] E' (tensile storage modulus) was measured at $T = 200°C$. C_{DCP} (concentration of the unreacted monomer) wt % of the monomer in the polymer sample.
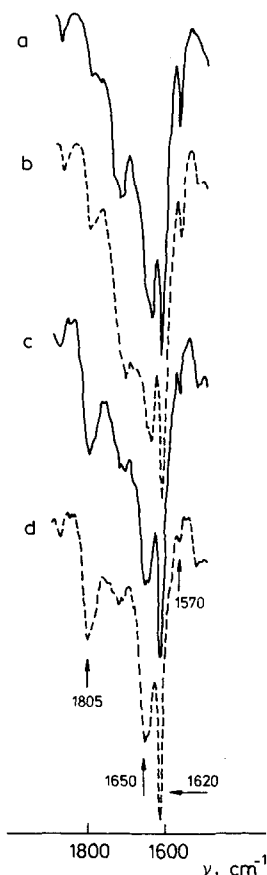
Fig. 8. IR spectra of thin polyDCP samples prepared by isothermal polymerization at various reaction temperatures (T_r): (a) $T_r = 25°C$; (b) $T_r = 90°C$; (c) $T_r = 145°C$; (d) $T_r = 210°C$.

DISCUSSION

Polymerization of DCP results in formation of a crosslinked polymer with high crosslink density. The polymer is formed without a significant consumption of the double bonds, which implies that the reaction proceeds by a metathesis type mechanism. NMR results obtained in Hercules Research Center show that possible consumption of the double bonds, if any, does not exceed 5% of conversion. The ATR method proved that the reaction is composed of several stages: induction period, first and second exotherm.

Induction Period

During the induction period, formation of catalytically active centers takes place. The inhibitor (dibutyl ether) extends the induction period, possibly by forming a complex with the catalyst which competes with the monomer activation. An alternative explanation is the formation of Al–alkyl complex which delays formation of an active catalyst. A small extent of reaction and even gelation within the induction period are due to the fact that some of the active centers "escape" the inhibitor effect, and thus initiate ring opening polymerization.
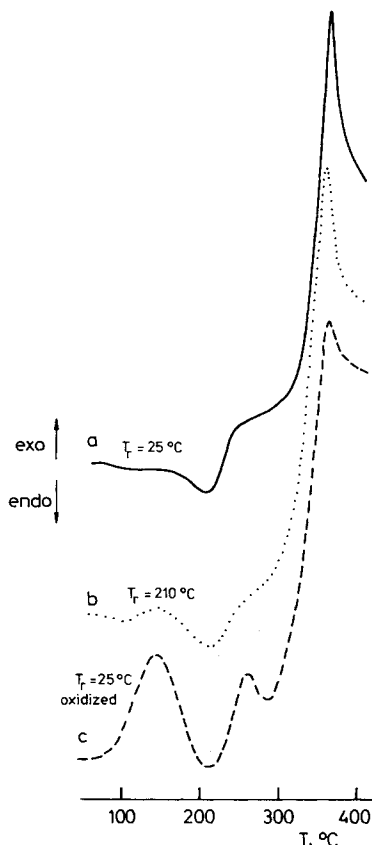
Fig. 9. DSC trace of thin polyDCP samples prepared by isothermal polymerization at different reaction temperatures (T_r): (a) $T_r = 25°C$; (b) $T_r = 210°C$; (c) $T_r = 25°C$, oxidized sample.

Gelation

The very low conversion at the gel point $\alpha_c < 0.01$ is evidence of a chainwise mechanism of the DCP polymerization. It means that the catalytic center initiates the chain growth resulting in a long kinetic chain. Consequently, migration of the catalyst, i.e., its regeneration and the initiation of another chain, is not very probable. Catalyst system works as an initiator rather than as a usual catalyst for which the regeneration is typical. Formation of long chains with pendant functionalities at a very early stage of the reaction results in gelation at a small reaction conversion. The slight increase in critical conversion α_c with dilution of the system indicates that there may be some cyclization. However, data are not precise enough for evaluation.

Crosslinking during the norbornene polymerization cannot proceed by metathesis because norbornene is monofunctional with respect to the ring opening polymerization. However, both catalyst components could also be effective as ionic catalysts, so that partial participation of a cationic mechanism in addition to the ring opening might explain the crosslinking. In fact, the slow polymer formation observed in a mixture of a monomer and of the cocatalyst component is possibly a result of a cationic polymerization.

From the analogy between the norbornene and DCP systems, we assume

that the same mechanism of crosslinking in the early stage of the reaction might be applied to the DCP polymerization: The reaction is initiated by the ring opening polymerization through the more strained norbornene ring of the DCP monomer and long linear chains are formed. Participation of the cationic reaction results in crosslinking. The analysis shows that a 0.01% conversion by the cationic reaction would be sufficient for gel formation. Consequently, the extent of the cationic reaction is very small and consumption of the double bonds is negligible. Contribution of the ring opening polymerization through the less reactive pendant cyclopentene rings cannot be excluded in this early stage (induction period). In a later stage, the crosslinking and formation of the polymer network structure take place by metathesis.

Exotherm

The exotherm of the reaction is composed of two parts as a result of at least two different reactions. Our results reveal the reaction temperature range for the optimum structure and properties of the cured samples. The temperature dependence of the structural parameters both in the "adiabatic" polymerization (T_{max}) and in the isothermal experiments ($T_{reaction}$) shows a maximum at 100–140°C. These two independent experiments prove that the final reaction temperature controls the quality of the polymer network. Some samples prepared under the conditions of large heat loss did not show the second exotherm (Fig. 2), but despite this fact they often show better structural parameters. Consequently, the temperature rise during the second exotherm results in a deterioration of the properties: decrease in the modulus (crosslink density) and increase in the sol fraction and in the amount of the unreacted DCP monomer.

Deterioration of the properties occurs only by heating the active system—containing the active catalyst—during the reaction. Heating the cured sample with an inactive catalyst results, in an increase in the modulus rather than a decrease (Table I). Hence, a degradation by metathesis type mechanism requiring the active catalyst system or a reduction of a conversion during the reaction at a higher temperature could account for the results.

We assume that the higher temperature results in a faster deactivation of the catalyst system and in reducing the reaction conversion leading to a lower crosslink density and higher sol fraction and amount of unreacted monomer.

Another effect is likely to contribute as well. The ring opening polymerization is an equilibrium and exothermic reaction. Thus, one can expect that the equilibrium composition monomer–oligomer–polymer will depend on the temperature and will be shifted towards the monomer at a higher temperature.[10] The depolymerization was proved in many linear metathesis polymerizations.[4,10] The intramolecular metathesis ("back biting") leads to the formation of a cycle (monomeric or larger) and a shorter linear chain. In our case this cyclodegradation reaction results in a decrease in crosslink density and increase in a sol fraction and content of unreacted monomer. The cyclization was suggested in a pregel stage of the DCP polymerization from an increase of α_c in dilute solutions. We assume that DCP is to some

small extent incorporated into the backbone of a primary chain also by its less strained cyclopentene ring (see Fig. 1, unit B). The cyclodegradation through this unit leads to the monomer in addition to the less probable norbornene ring (Fig. 1, unit A) closure. The cyclopentene ring in DCP is slightly reactive,[11] but the high crosslink density of our networks reveals its ring opening polymerizability. Also, Dall'Asta mentioned the metathesis reaction of this ring in DCP in some cases.[9]

Our crosslinked system does not seem to reach the equilibrium because of the slowing down of depolymerization at a later stage of the reaction. The concentration of the unreacted monomer is controlled kinetically. Despite this fact, its higher content at higher temperature is to be expected.

First Exotherm

The first exotherm on the ATR plots involves the metathesis polymerization through both the norbornene and cyclopentene rings. The cationic reaction mechanism does not contribute to the overall conversion in a significant way. The enthalpy of the reaction (ΔH_1 = first exotherm) in adiabatic systems is $\Delta H_1 = C_p \Delta T_1 = 10$ kcal/mol deg (ΔT_1 is a temperature rise in the first exotherm). Unlike the very exothermic opening of the more strained norbornene ringe, crosslinking through the pendant cyclopentene rings is less exothermic.[12,13] Consequently, ΔH_1 corresponds mainly to the opening of the norbornene ring. During this first exotherm, a maximum reaction conversion and a maximum crosslink density of the network were reached. Under the optimum conditions about 50% of units in the polymer are crosslinked. We take into account the crosslink density calculated from the modulus of the mold runner ($\nu = 7.0$–9.2×10^{-3} mol/cm^3) and the theoretical value: $\nu_{th} = 15.2 \times 10^{-3}$ mol/cm^3.

Second Exotherm

During the second exotherm, degradation takes place. As the depolymerization is an athermic or even slightly endothermic process, another exothermic reaction must occur in addition to cyclodegradation so that the second exotherm may be explained. So far the nature of this reaction is not clear and more study is necessary. One might take into account the thermal-activated radical reactions involving a chain structure rearrangement or an oxidative formation of peroxides at a high temperature followed by radical reactions. The former idea assumes that the thermal decomposition of the part of the catalyst system—acetyl acetonate—occurs during a temperature rise,[14] initiating a radical exothermic ring splitting.[15] A very complex set of exothermic Diels–Alder type reactions can follow:
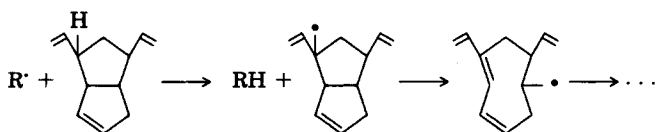
The hypothesis of peroxide formation comes from a similar thermal behavior of the samples prepared at a high temperature and of the oxidized

samples. Both show a new exotherm at 150°C in DCS thermograms assigned to a decomposition of peroxides and to subsequent radical reactions. Also, the IR band at 1805 cm^{-1} of the samples prepared at a high temperature might correspond to a carbonyl attached to a highly strained ring arising by decomposition of peroxides. There is only a trace content of oxygen in the system, so that oxidation could serve only as initiator of the exothermic process.

The temperature rise due to an exothermic reaction during the second exotherm discussed above favors cyclodegradation.

Interpretation of Experimental Data

The experimental results can be explained on the basis of the proposed mechanism as follows: The dependence of the content of the unreacted monomer and of the gel fraction on the reaction temperature (Figs. 4 and 6) shows three regions. In the temperature region I the sample is not completely cured because of a diffusion control during the reaction at a temperature in the vicinity of T_g or even below T_g (compare Table II). The monomer content in the polymer and the sol fraction increase in the region II is a result of the depolymerization or/and faster catalyst deactivation. Evaporation of DCP and the dissociation DCP → cyclopentadiene above the boiling point of DCP (T_b = 171°C) lead to a decrease in content of the unreacted monomer in the region III. The monotonic decrease in crosslink density at a higher temperature proves that the degradation continues and that the region III does not correspond to the additional DCP polymerization. Also, the increase in T_g at a high temperature is a result of the monomer leaving. The monomer evaporation during the reaction can be seen in ATR plots as a small endotherm at 180°C (Fig. 2). Also, the strong decrease in IR absorption bands at 1570 cm^{-1} at the reaction temperature above 170°C (Fig. 8) is due to the DCP disappearance. Even the cured samples release the remaining monomer on heating as was observed in DSC measurements—endotherm at 210°C. The weight loss associated with this endotherm, and the dissapearance of the peak at the rescan corroborates the idea.

Oxidation affects the surface of the sample. Consequently, the bulk properties (modulus) of the thin samples are much more susceptible to oxidation than properties of the thick "adiabatic" samples.

CONCLUSION

The dicyclopentadiene polymerized by the reaction injection molding (RIM) technique using the Ziegler–Natta type catalyst formed a highly crosslinked polymer. The fast and exothermic reaction proceeds by the matathesis mechanism through both the norbornene and cyclopentene rings. Some participation of the cationic mechanism in the early stage of the reaction is possible. The onset of the main polymerization (exotherm) may be delayed with an inhibitor. However, gelation occurs already within the induction period because of imperfect inhibition and a very low critical conversion at the gel point. The two exotherms of the reaction correspond to the ring opening polymerization and to an unknown exothermic reaction,

the nature of which is discussed. The polymer structure and properties are dependent on the reaction temperature. Too high temperature results in deterioration of the sample properties due to cyclodegradation and/or the catalyst deactivation. The optimum reaction temperature is 100–140°C.

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