

Preparation and Properties of Polycarbodiimides

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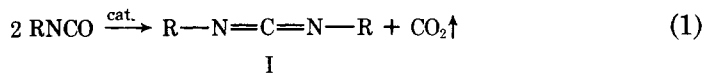
Synopsis

A series of polycarbodiimides was prepared from isocyanates using 1-phenyl-3-methyl-2-phospholene-1 oxide as catalyst. The molecular weight of the series was varied by employing controlled amounts of phenyl isocyanate as a terminating agent. The resultant polymers showed improved processing over very high molecular weight unterminated polymer, while still maintaining good thermal stability and equivalent mechanical properties. A study of the viscoelastic properties of these polymers using modulus-temperature plots showed that the materials underwent a crosslinking reaction at elevated temperatures (200–250°C). These reactions could be explained on the basis of a model, diphenylcarbodiimide, and most likely include the formation of carbodiimide dimers and trimers.

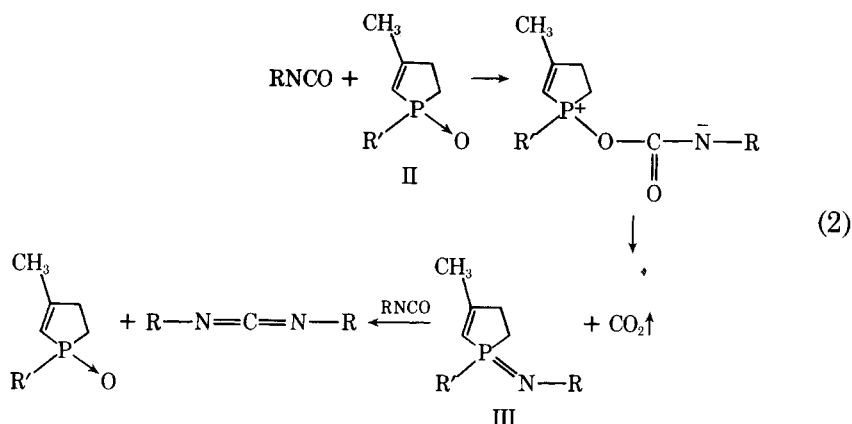
INTRODUCTION

Although the formation of carbodiimide has been known for some time, these materials have not received a great deal of attention until relatively recently. The usual methods of preparation¹ generally were multistep processes which were somewhat cumbersome. Polycarbodiimides have received increased attention in recent years because of the ease of their preparation using phospholene oxide catalysts, and their excellent thermal and oxidative resistance has suggested their use as a high-temperature engineering plastic.^{2,3,4,5}

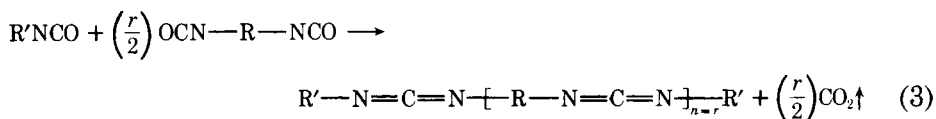
The overall reaction consists of an isocyanate function reacting with another isocyanate to yield carbodiimide (I) and carbon dioxide:



The role of the catalyst and the mechanism also have been studied,⁶ and involves the reaction of the phospholene oxide catalyst (II) with an isocyanate to give a phosphinimine (III) and carbon dioxide. The phosphinimine then reacts with another isocyanate to give the carbodiimide and regenerate the catalyst as it appears on overleaf (2). The overall reaction is quite rapid and produces carbodiimides in high yields. Such a reaction is ideal for forming polymer, as very high molecular weight is obtained under mild conditions. These polymers have been found to have useful high-temperature properties.^{7,8} The carbodiimide reaction also has been used in the preparation of urethane elastomer copolymers^{9,10,11} and in rigid foams.^{12,13}



The high molecular weight linear polycarbodiimides are insoluble and somewhat difficult to process.⁸ For this reason, various techniques have been used to overcome these problems,^{8,11,14} but they have resulted in limited success. The purpose of this research was to determine ways to improve the processability of carbodiimide polymers. The main method used was to limit molecular weight through the addition of specified amounts of monofunctional isocyanates. As shown in eq. (3), this terminated the polymer chains with endgroups which were equal in thermal stability to the backbone of the polymer. The ratio of equivalents of difunctional isocyanate to monofunctional isocyanate (r) was varied from 3/1 to 50/1. Unterminated polymer ($r = \infty$) also was prepared:



The theoretical number-average degree of polymerization, n , is equal to the ratio r . It was surprising to find that the polymers prepared in the range of D.P. of $r = 6/1$ to $r = 20/1$ had mechanical properties very nearly equal to those of high molecular weight unterminated polymers.

EXPERIMENTAL

The hydrocarbon solvents used were dried by azeotroping off the water and were stored over molecular sieves. The diisocyanate used was Upjohn's 125MF 4,4'-diisocyanatodiphenylmethane (MDI), and it was used as received. The monofunctional isocyanates used were phenyl, *p*-methoxyphenyl, *o*-tolyl, and 2,6-diethylphenyl. They were technical grade and were used as received. The catalyst used was 1-phenyl-3-methyl-2-phospholene-1 oxide, and it was prepared and purified according to procedures in the literature.¹⁵

The general polymerization procedure consisted of adding the desired amounts of MDI and monofunctional isocyanate to a resin flask with the solvent. The solution then was heated to the desired temperature and the catalyst added from a stock benzene solution (usually 0.3 g catalyst per equivalent of isocyanate). The reaction immediately began with the evolution of carbon dioxide. The course of the reaction was followed by measuring the carbon dioxide evolution

with an American Meter Company gas meter. At the end of the gas evolution, infrared measurements were made to determine when all the isocyanate had reacted (2270 cm^{-1}). The carbodiimide peak at 2130 cm^{-1} could readily be observed. In some experiments, as indicated in Table I, polymer would precipitate. This was filtered off, dried, and weighed in order to determine the percentage of soluble material. In most cases, the solution or slurry was poured into an excess of hexane, and the bulk of the sample was collected as precipitated polymer. All the polymer powders were air dried and then vacuum dried 6 hr at $100\text{--}110^\circ\text{C}$ before any further processing or tests were run.

DTA and TGA thermograms were obtained on the powder samples using a du Pont 900 thermal analyzer. Number-average molecular weight measurements were made on a Hewlett-Packard VPO. Samples were compression molded on a Wabash 30-ton hydraulic press equipped with heated platens, and modulus-temperature measurements were made on a modified Gehman torsional stiffness tester. Melt processing studies were performed using a Brabender Palsti-Corder equipped with a measuring head and an extruder.

RESULTS AND DISCUSSION

Table I contains a listing of various phenyl isocyanate-terminated polycarbodiimides. The reactions in xylene were run at 120°C , while those in benzene were run at $70\text{--}75^\circ\text{C}$. The per cent soluble polymer is that fraction which remained in solution. The second part of Table I lists the per cent powder recovered from precipitating the polymerization solution or slurry into hexane. The yields are nearly quantitative, and the remainder stays as very low molecular weight products in the solvent/nonsolvent wash. The data in Table I show that solubility decreases as molecular weight increases.

TABLE I
Phenyl Isocyanate-Terminated Polycarbodiimides

Sample	Equiv. MDI/ equiv. ϕNCO	Solvent	Yield	
			% Soluble	% Insoluble
1	3/1	X ^a	91	9
2	4/1	X	88	12
3	5/1	X	79.3	21.7
4	6/1	X	17.4	82.6
5	10/1	X	11.4	88.6
6	50/1	X	5	95
			% Powder recovered	
7	3/1	X		80.6
8	10/1	X		95
9	10/1	X		93.5
10	10/1	B/H ^b		93.8
11	12/1	X		94.6
12	20/1	B		97.9
13	20/1	B/H		96
14 (222-428)	∞	X		98.5
15	∞	X		94

^aX = xylene.

^bB = benzene; H = hexane.

TABLE II
 Polymers Terminated at Ratio of 15/1

Sample	Monofunctional NCO	Yield, % powder
16	Phenyl	93
17	<i>o</i> -Tolyl	92
18	<i>p</i> -Methoxyphenyl	98
19	2,6-Diethylphenyl	95

Also included in Table I are several runs for unterminated polymers, $r = \infty$ (samples 14 and 15). As can be seen from Table I, the percent of recovered powder is nearly the same for unterminated as for terminated where $r \geq 10/1$.

VPO measurements on a sample for $r = 5/1$ yielded a value of $\bar{M}_n = 1346$ versus 1224 for the theoretical value. The experimental value is somewhat higher due to the loss of lower molecular weight species in the solvent/nonsolvent wash. The η_{inh} (0.5%, CHCl_3) was 0.09.

A 10/1 sample had an η_{inh} in N-methylpyrrolidinone of 0.15. This solvent could not be run on the VPO.

Table II lists some terminated polymers at $r = 15/1$ for the various monofunctional isocyanates used. The yields are nearly the same regardless of terminating agent, and the polymers appeared the same in all other respects.

The TGA data for these polymers were obtained in air at 15°C/min, and are shown in Table III. As one might expect, at lower ratios, a larger amount of volatile lower molecular weight material is present, which shows up as a higher weight loss at temperatures less than 400°C. At 400°C, catastrophic decomposition occurs, and the TGA results cannot be interpreted on the basis of molecular weight, since some of the polymers softened and deformed on the sample pan.

These terminated polycarbodiimides could easily be compression molded. Table IV lists the molding conditions and tensile strengths of various terminated and unterminated polymers. The table shows that the terminated polymers can be molded at lower temperatures and somewhat lower pressures than the unterminated polymers. What is interesting is that the tensile strengths are somewhat better. This may be due to better molding, which can be achieved with the terminated polymers.

Since the purpose of this research was to produce oligomers which would be more processable than unterminated polymers, various methods must be used

 TABLE III
 Terminated Polycarbodiimides TGA Data in Air. Heating Rate 15°C/min

Sample	Ratio	Cumulative % weight loss				
		200°C	300°C	400°C	500°C	600°C
7	3/1	1.9	7.3	8.5	43.0	56.0
9	10/1	0.1	0.7	0.8	1.5	79.0
16	15/1	0	0.9	1.3	2.5	64.0
12	20/1	0.2	1.0	1.2	2.4	26.0
6	50/1	0	0.6	2.4	14.0	50.0
14	∞	0	0	1.0	6.0	38.0

TABLE IV
Moldings on Terminated Polycarbodiimides

Sample	Ratio	Mold temp., °C	Pressure, psi	Tensile strength, psi
3	5/1	180–200	2500	11,500
4	6/1	200–220	2500	10,900
5	10/1	200–220	2500	11,000
11	12/1	180–200	2600	11,300
16	15/1	180–200	2600	11,300
17	15/1	180–200	2600	10,900
18	15/1	180–200	2600	11,300
12	20/1	180–200	2600	9,800
14	∞	250–260	3000	9,500
15	∞	250–260	4000	9,500

to evaluate any improvement. One convenient way of doing this is by using laboratory processing equipment such as a Brabender Plasti-Corder. Processing data using the mixing head on the Brabender is contained in Table V. All the powder samples had been vacuum dried 6 hr at 100–110°C. The unterminated polymer, sample 15, cannot be fluxed at all, while the oligomeric sample 7 can be fluxed readily at temperatures of 240–270°C. The torque readings, in meter-grams, show that, as would be expected, an increase in molecular weight causes an increase in melt viscosity. Several questions are raised by these experiments. It is not apparent from these data why the unterminated material cannot be fluxed. Also, sample 7, the 3/1 oligomer, first melts and then becomes rubbery, with a corresponding increase in melt viscosity. This gives some indication that changes are occurring in the viscoelastic properties of the material. Therefore, it is interesting to look at the viscoelastic properties by determining the change in modulus with temperature, as measured on a modified Gehman torsion stiffness tester. Such a plot is shown in Figure 1 for unterminated polymer. This plot shows that the material passes through a glass transition at approximately 220°C and goes into a rubbery region at approximately 250°C. However, it then stiffens and the modulus increases, and it is for this reason that it cannot be processed on the Brabender.

An isothermal study at 220.5°C shows in more detail what is occurring. These data are plotted versus time in Figure 2. On first heating, the modulus increases with time. The sample was cooled and reheated. It starts from where the

TABLE V
Brabender Mixing Head Studies

Sample	Ratio	rpm	Temp., °C	Torque, meter-g	Elapsed time, min
15	∞	low	250–275	—	4 jammed
7	3/1	40	230	50	5 melting
		40	240	2500	10 rubbery
		68	270	400	15–30 fluxing
9	10/1	50	270	3500	6 melting
		40	275	2700–2900	20 fluxing
11	12/1	30	275	2200–3900	10 fluxing
		60	280	3100–3500	20 fluxing
12	20/1	30	275	5300–6300	20 fluxed

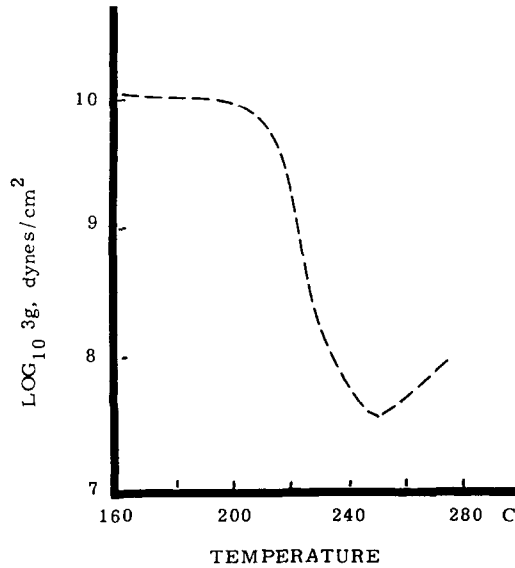


Fig. 1. Sample 222-428, molded.

original sample left off, showing that the process is irreversible with temperature. Such a linear increase in modulus with time would indicate that crosslinking is occurring.

The modulus-temperature plots also show the differences due to molecular weight in the series of polymers. Figure 3 compares 10/1 and 20/1 oligomers with 50/1 polymer and unterminated polymer. Sample 14 (Fig. 3) is unterminated polymer and shows that the effect of further heat treatment is to increase the modulus in the rubbery region. Sample 6, which is 50/1 polymer, behaves very similarly to unterminated polymer. Sample 12, which is 20/1 polymer, is interesting because the effect of annealing at 150–160°C increases the glass tran-

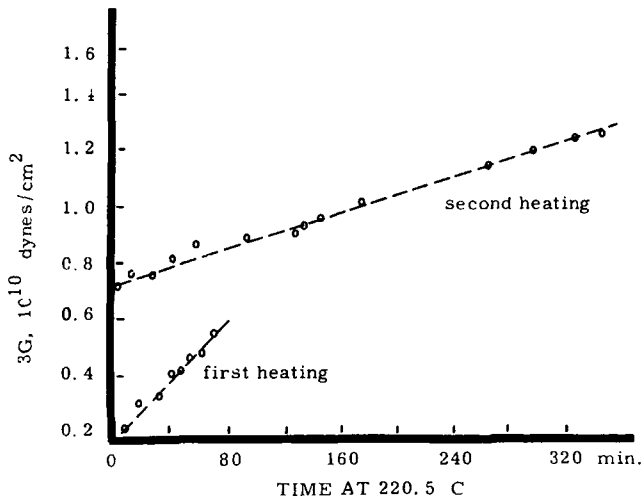


Fig. 2. Sample 222-428, molded.

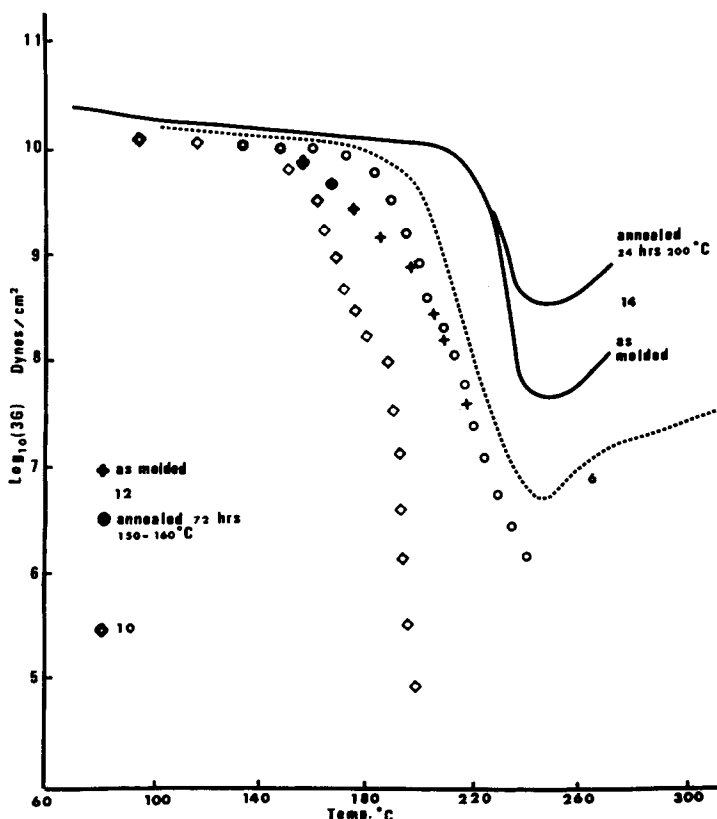


Fig. 3. Modulus-temperature plots.

sition of the material but does not affect the rubbery region. This point will be discussed further.

Finally, sample 10, which is 10/1 polymer, exhibits further evidence for the effect of molecular weight on the viscoelastic properties. These curves show that the 10/1 and 20/1 polymers are processable because their lower molecular weight allows them to be processed at a temperature below which rapid changes in molecular weight are occurring.

Heat treatment of the raw polymer powder also causes changes in some of the thermal properties of the material. Figure 4 contains two DTA scans and a TGA scan on 10/1 oligomer. The uppermost DTA scan was done on raw powder which has been vacuum dried 6 hr at 100–110°C. It shows an endotherm at ca. 132°C and the major transition at ca. 210°C. Upon cooling and reheating (the rescan on Fig. 4), the DTA scan no longer shows the endotherm, but still shows the major transition at 200–210°C. The lower curve in Figure 4 is a TGA scan of 10/1 oligomer which has been vacuum dried at 100–110°C for 6 hr. Since there is no evidence of any volatiles up to 160°C, the endotherm which is irreversible is not due to weight loss, but to some other event which is occurring.

Figure 5 shows an IR scan (KBr pellet) for powder vacuum dried for 6 hr at 100°C and for the same sample which was heated for 40 min further in an air oven at 150°C. The original scan shows the carbodiimide absorption at 2130 cm^{-1} .

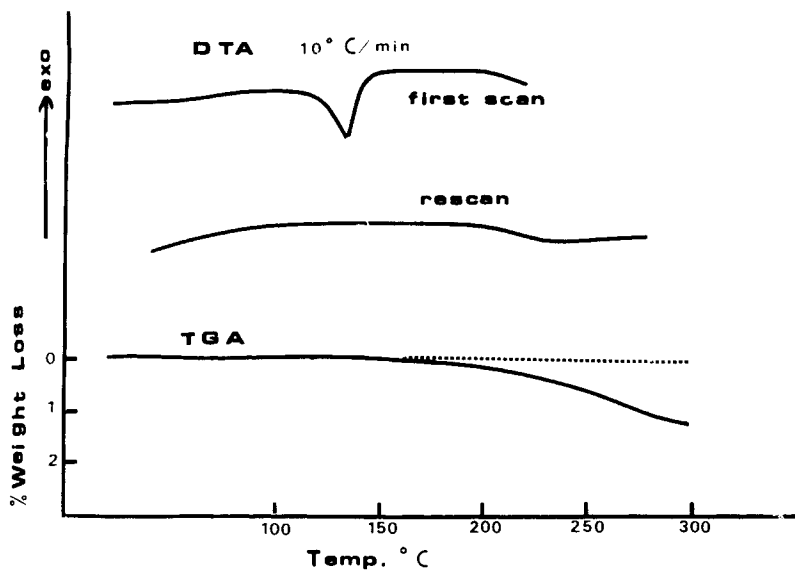


Fig. 4. DTA and TGA scan.

Upon heating further for 40 min at 150°C, there is a decrease in the intensity of the carbodiimide absorption band and the appearance of a new band at 1690 cm^{-1} , which is within the range (1700–1675 cm^{-1}) reported for the cyclic dimers and trimers of carbodiimides.^{17,18}

Finally, Table VI shows changes which occur in the mechanical properties of 20/1 polymer which has been further heated 18 hr at 150°C after drying in a

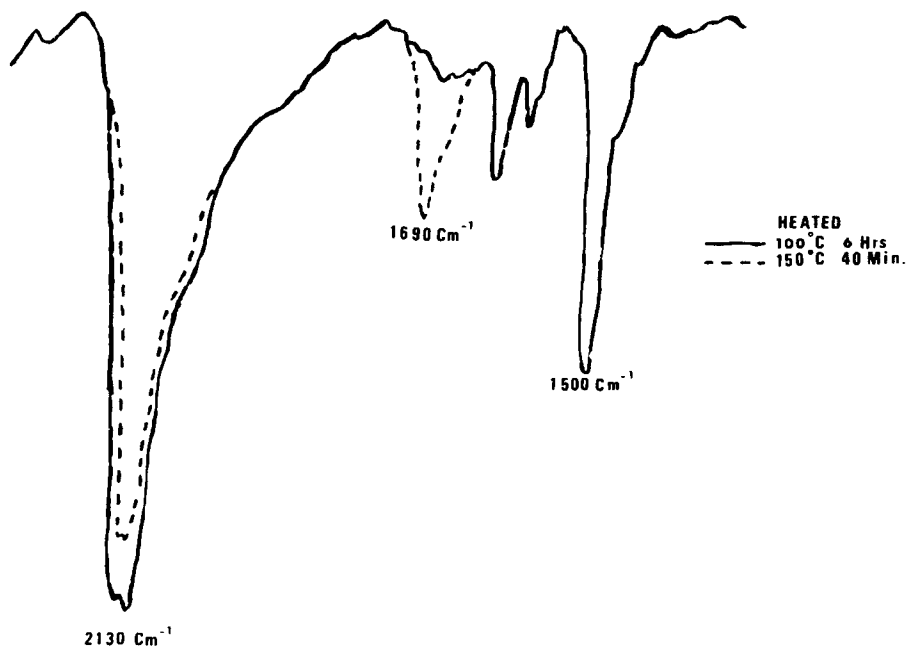


Fig. 5. IR scan, terminated 20/1.

TABLE VI
 Heat-Treated 20/1 Polycarbodiimide

	As molded	Heated 150°C, 18 hr
Tensile strength, psi	10,800	10,300
Modulus, psi	264,400	258,150
Elongation, %	7.3	5.2

vacuum oven for 6 hr at 100–110°C. The main difference is a decrease in the elongation of the sample after heat treatment, while the modulus is changed very little.

Thus far, we have shown that heat treatment causes changes in the thermal properties, mechanical properties, viscoelastic properties, and the infrared of the carbodiimide polymers, but we have only hinted at what may be the cause of the changes.

Since we know that a polymer consists of a statistical distribution of molecular weights, then, for polymers in the range of 6/1 to 20/1, there is a significant amount of low molecular weight material—even some diphenylcarbodiimide. These lower molecular weights can act as plasticizers and thus allow the polymers to be processed. However, the carbodiimide function can react with itself.^{16,17,18} Thus, during processing and heat treating, these reactions can take place. First, at low temperatures, melting of lower molecular weight material would occur, as demonstrated by the first DTA scan of Figure 4; and as the temperature is increased and larger chains become more mobile, all segments can take part in the reactions. The lower molecular weight material which first melts can then form dimer and trimer of the carbodiimide, giving rise to the new peak at 1690 cm^{-1} (Fig. 5). Some of these structures that could be formed could give rise to crosslinking which would increase the modulus, especially in the rubbery region. As shown from Figure 2, at 220.5°C there are enough bonds formed to significantly raise the modulus.

Some of these structures which can form, using diphenylcarbodiimide as a model, are shown in Figure 6 with their melting points.^{17,18} Although the melting points are higher than that seen in the first DTA scan (Fig. 4, 132°C), these are for pure model compounds, and it might be expected that in a polymer matrix, the melting points would be lowered. Although the dimer is reversible, even a small amount in equilibrium would give rise to crosslinking since the carbodiimide bond is in the backbone of the polymer chain.

In summary, we have shown that controlling the molecular weight by terminating the polymer to form what is actually oligomer leads to a more processable

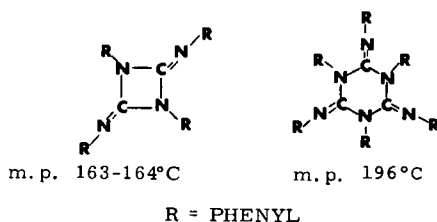


Fig. 6. Diphenylcarbodiimide dimers and trimers.

polymer. Because of the unusual reactive nature of the carbodiimide, these oligomers have unusually high strengths for such low apparent molecular weight. Heat treatment has been shown to cause further reactions to occur which produce changes in the mechanical and viscoelastic properties of the oligomers.

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