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The Synthesis and Polymerization Studies of Some Higher Homologues of 9-Vinylcarbazole

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SUMMARY:

9-Allylcarbazole, 9-Δ^3-butenylcarbazole, 9-Δ^4-pentenylcarbazole and 9-Δ^5-hexenylcarbazole were synthesized and their polymerization with Ziegler-Natta catalyst systems studied. 9-Allylcarbazole could not be polymerized and 9-Δ^3-butenylcarbazole could only be polymerized with extreme difficulty. However, 9-Δ^4-pentylcarbazole and 9-Δ^5-hexenylcarbazole could be polymerized at conversions of about 55%. These results are interpreted in terms of steric hindrance about the vinyl group. No evidence of complexing due to the basic nitrogen atom was noted. Of the catalyst systems used only Et_2AlCl-$\gamma TiCl_3$ was found to be effective in the polymerization. As judged by X-ray diffraction and insolubility the polymers were highly crystalline.

ZUSAMMENFASSUNG:

9-Allylcarbazol, 9-Δ^3-Butenylcarbazol, 9-Δ^4-Pentenylcarbazol und 9-Δ^5-Hexenylcarbazol wurden synthetisiert, und ihre Polymerisation mit Ziegler-Natta-Katalysatorsystemen wurde untersucht. 9-Allylcarbazol ließ sich nicht polymerisieren, und 9-Δ^3-Butenylcarbazol konnte nur unter großen Schwierigkeiten polymerisiert werden. Dagegen wurden 9-Δ^4-Pentenylcarbazol und 9-Δ^5-Hexenylcarbazol zu Umsätzen von ca. 55% polymerisiert. Die Ergebnisse werden durch sterische Hinderung an der Vinylgruppe erklärt. Komplexbildung durch das basische Stickstoffatom wurde nicht beachtet. Von den benutzten Katalysatorsystemen war nur Et_2AlCl—$\gamma TiCl_3$ polymerisationsaktiv. Aus Röntgenspektren und Unlöslichkeit wurde auf eine hohe Kristallinität der Polymeren geschlossen.

1. *Introduction*

In a previous paper we have described our attempts to achieve a stereoregulated polymerization of 9-vinylcarbazole by means of certain Ziegler-Natta catalyst systems and have shown that under the conditions investigated only atactic, noncrystalline polymers could be obtained[1]. The failure to achieve a stereoregulated polymerization was attributed to the great ease with which 9-vinylcarbazole undergoes a nonstereospecific cationic polymerization due to the Lewis-acid character of the catalyst mixture.

Since the ease of cationic polymerization is due to the conjugation of the vinyl group with the carbazole aromatic system, it became of interest to synthesize and to study the polymerization of a number of higher homologues of 9-vinylcarbazole where this conjugation has been destroyed. The present paper describes such a study carried out with 9-allylcarbazole, 9-Δ^3-butenylcarbazole, 9-Δ^4-pentenylcarbazole and 9-Δ^5-hexenylcarbazole.

2. *Experimental*

A. *Synthesis of monomers*

a) 9-allylcarbazole (I)

This compound was prepared from sodium carbazole and allyl bromide in tetrahydrofuran. This synthesis was found more convenient than the previously described[2] condensation of potassium carbazole and allyl iodide.

Sodium carbazole was prepared by the dropwise addition of 20 g. (0.12 mole) of carbazole in 150 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) to a suspension of 5.6 g. (0.13 mole) of sodium hydride (53.1% dispersion in mineral oil) in 120 ml. tetrahydrofuran. The mixture was stirred until no more hydrogen was evolved and then heated to reflux. To this refluxing solution was added dropwise 15.4 g. (0.12 mole) of freshly distilled allyl bromide and the reflux continued overnight. The cooled reaction mixture was then poured into 500 ml. of water, extracted with three 100 ml. portions of ether and the combined ether extracts dried over anhydrous magnesium sulfate. The ether was evaporated and the residue recrystallized from methanol to yield 14.4 g. (58.0%) of a pale brown solid, m.p. 53–55 °C. Sublimation of this material (100 °C., 0.2 mm. Hg) gave a white product, m.p. 54–55 °C. (56 °C.[2]). Its NMR signal consisted of a multiplet (1,8-carbazole hydrogens) at $\tau = 1.8$–2.0, a multiplet (2,3,4,5,6,7-carbazole hydrogens) at $\tau = 2.3$-2.9, a multiplet (internal vinyl hydrogen) at $\tau = 3.7$–4.4 and a multiplet (N–CH_2) at $\tau = 5.1$–5.3.

$C_{15}H_{13}N$ (207.26)	Calcd.	C 86.92	H 6.32	N 6.76
	Found	C 87.27	H 6.64	N 6.80

b) 9-Δ^3-butenylcarbazole (II)

This compound was prepared by the condensation of sodium carbazole and 1,4-dichlorobutane or 1,4-dibromobutane, the conversion of the resulting 9-(4-chlorobutyl)carbazole or 9-(4-bromobutyl)carbazole to 9-(4-N,N-dimethylaminobutyl)carbazole, which was then oxidized to the amine oxide and pyrolyzed. A synthesis *via* the condensation of sodium carbazole and 4-bromo-1-butene was not possible because of the preferred dehydrohalogenation reaction leading to 1,3-butadiene.

9-(4-chlorobutyl)carbazole.

Sodium carbazole was prepared as described before from 8.3 g. (0.05 mole) of carbazole in 55 ml. of tetrahydrofuran and 2.8 g. (0.061 mole) sodium hydride (53.1% dispersion in mineral oil) in 60 ml. tetrahydrofuran. The sodium salt was then transferred to a dropping funnel and added dropwise to a stirred mixture of 73.0 g. (0.57 mole) of 1,4-dichlorobutane, 60 ml. of tetrahydrofuran and a small amount of potassium iodide, maintained at 70–75 °C. Stirring and heating was continued for an additional 18 hrs. The cooled reaction mixture was then poured into 500 ml. water, extracted with three 60 ml. portions of ether and the combined ether extracts dried over anhydrous magnesium sulfate. The solvent, along with unreacted 1,4-dichlorobutane, was removed by vacuum distillation and the solid residue recrystallized from 300 ml. of methanol to yield 8.2 g. (63.6%) of a pale brown solid, m.p. 92–95 °C. Vacuum sublimation (130 °C., 0.1 mm. Hg) gave a white product, m.p. 96–97 °C.

$C_{16}H_{16}NCl$ (257.71)	Calcd.	C 74.55	H 6.26	N 5.43	Cl 13.76
	Found	C 74.81	H 5.79	N 5.45	Cl 13.48

9-(4-bromobutyl)carbazole

According to the same technique as before, 4.1 g. (0.025 mole) of carbazole in 30 ml. tetrahydrofuran was added to a suspension of 1.4 g. (0.032 mole) of sodium hydride (53.1% dispersion in mineral oil) in 30 ml. tetrahydrofuran. This sodium salt was then treated with 54.0 g. (0.25 mole) of 1,4-dibromobutane in 25 ml. tetrahydrofuran, yielding 6.2 g. (83.0%) of a pale yellow solid. Vacuum sublimation (140 °C., 0.2 mm. Hg) gave a white product, m.p. 105–106.5 °C.

$C_{16}H_{16}NBr$ (302.17)	Calcd.	C 63.18	H 5.34	N 4.64	Br 26.44
	Found	C 63.76	H 6.57	N 4.63	Br 26.32

9-(4-N,N-dimethylaminobutyl)carbazole

A mixture of 12.08 g. (0.04 mole) 9-(4-bromobutyl)carbazole, 20 ml. dioxane and 20 ml. (0.30 mole) dimethylamine were sealed into a glass tube and the tube heated in a steam-cone for 12 hrs. The tube was then opened and the contents poured into 120 ml. of water and extracted with three 40 ml. portions of benzene. The combined benzene extracts were dried over anhydrous magnesium sulfate and then saturated with anhydrous hydrogen chloride. A heavy oil formed which was separated and dissolved in water. The water solution was made basic with 10% sodium hydroxide, extracted with three 40 ml. portions of ether and the combined ether extracts dried over anhydrous magnesium sulfate. The solvent was then evaporated and the residue cooled in dry ice to induce crystallization. The yield was 7.0 g. (66.0%) m.p. 45.5–46 °C.

$C_{18}H_{22}N_2$ (266.37)	Calcd.	C 81.15	H 8.33	N 10.52
	Found	C 80.96	H 8.29	N 10.69

9-(4-N,N-dimethylaminobutyl)carbazole oxide

To a solution of 6.7 g. (0.025 mole) 9-(4-N,N-dimethylaminobutyl)carbazole in 55 ml. of absolute methanol was added 3.0 ml. (0.033 mole) 30% hydrogen peroxide and the solution allowed to stand at room temperature. Additional 3.0 ml. (0.038 mole) portions of 30% hydrogen peroxide were added after 1 and 5 hrs. reaction time. The reaction mixture was then allowed to stand until no color developed on testing 1 drop of the reaction mixture in 3 drops of water with 1 drop of alcoholic phenolphthalein solution[3]. The excess peroxide was decomposed with 10% palladium on charcoal*), the mixture filtered and the solvent removed. The amine oxide remained as a reddish, viscous syrup and was used without purification.

9-(4-N,N-dimethylaminobutyl)carbazole oxide picrate

$^1/_2$ ml. of the amine oxide was dissolved in 10 ml. of 95% ethanol and this solution added to 20 ml. of a saturated solution of picric acid in 95% ethanol. A pure monopicrate was obtained by repeated crystallization from 95% ethanol, m.p. 175–177 °C.

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*) Extreme caution should be exercised at this step since a violent explosion can result. The Pd/C should be added as a methanol slurry and the reaction mixture should be maintained under a nitrogen atmosphere.

$C_{24}H_{25}N_5O_8$ (371.30) Calcd. C 56.35 H 4.93 N 13.69
Found C 55.98 H 4.61 N 13.90

9-Δ^3-butenylcarbazole (II)

The amine oxide was placed in a 100 ml. round bottom flask connected to a dry ice-acetone trap, the system evacuated to 0.1 mm. Hg and the flask slowly heated in an oil bath. After the initial vigorous decomposition subsided the bath temperature was raised to 150 °C. and maintained at that temperature for 0.5 hr. The cooled residue in the flask and the solid contents of the trap were dissolved in 60 ml. of ether, washed successively with 10 % hydrochloric acid, 5 % sodium bicarbonate, water and then dried over anhydrous magnesium sulfate. The solvent was next evaporated and the oily residue cooled in dry ice to induce crystallization. The resulting solid was recrystallized from methanol, which on cooling to –78 °C. yielded 4.2 g. (76.5 %) of product m.p. 43.5–45 °C. Its NMR signal consisted of a multiplet (1,8-carbazole hydrogens) at τ = 1.9–2.2, a multiplet (2,3,4,5,6,7-carbazole hydrogens) at τ = 3.8–4.6, a multiplet (terminal vinyl hydrogens) at τ = 4.7–5.2, a triplet (N–CH_2) at τ = 5.75 and a quartet (allylic hydrogens) at τ = 7.47.

$C_{16}H_{15}N$ (221.29) Calcd. C 86.84 H 6.83 N 6.33
Found C 86.75 H 6.41 N 6.47

c) 9-Δ^4-pentenylcarbazole (III)

According to the same technique as that described under I, 16.72 g. (0.1 mole) of carbazole in 150 ml. of tetrahydrofuran was added dropwise to a suspension of 5.8 g. (0.12 mole) of sodium hydride (53.1 % dispersion in mineral oil) in 100 ml. of tetrahydrofuran. The reaction mixture was then heated to reflux and 74.5 g. (0.5 mole) of 5-bromo-1-pentene slowly added. After refluxing for 15 hrs., cooling and pouring into 500 ml. of water, the reaction product was extracted with three 100 ml. portions of ether and the combined extracts dried over anhydrous magnesium sulfate. Excess ether and 5-bromo-1-pentene were removed by distillation, the solid residue dissolved in hexane, insolubles filtered off, evaporated to dryness, and product recrystallized from methanol to yield 10.4 g. (68 %) of white needles, m.p. 46.6–47 °C. Its NMR signal consisted of a multiplet (1,8-carbazole hydrogens) at τ = 1.9–2.2, a multiplet (2,3,4,5,6,7-carbazole hydrogens) at τ = 2.6–3.1, a multiplet (internal vinyl hydrogen) at τ = 4.0–4.7, a multiplet (terminal vinyl hydrogens) at τ = 4.8–5.2, a triplet (N–CH_2) at τ = 5.8 and a multiplet (2 methylenes) at τ = 7.8–8.3.

$C_{17}H_{17}N$ (235.32) Calcd. C 86.76 H 7.28 N 5.96
Found C 86.57 H 7.61 N 5.74

d) 9-Δ^5-hexenylcarbazole (IV)

According to the same technique described under I, 16.72 g. (0.1 mole) of carbazole in 150 ml. of tetrahydrofuran was added dropwise to a suspension of 5.8 g. (0.12 mole) of sodium hydride (53.1 % dispersion in mineral oil) in 100 ml. of tetrahydrofuran. The reaction mixture was then heated to reflux and 81.5 g. (0.5 mole) 6-bromo-1-hexene slowly added. After refluxing for 15 hrs. cooling and pouring into 500 ml. of water, the reaction product was extracted with three 100 ml. portions of ether and the combined ether extracts dried over anhydrous magnesium sulfate. Excess ether and 6-bromo-1-hexene were removed by distillation, the solid residue dissolved in hexane, insolubles filtered off, evaporated to dryness and product recrystallized from methanol to yield 14.1 g. (56.5 %) of white needles, m.p. 76–76.5 °C. Its NMR signal consisted of a multiplet (1,8-carbazole hydrogens) at τ = 1.9–2.2, a multiplet (2,3,4,5,6,7-carbazole hydrogens) at τ = 2.6–3.1, a multiplet (internal vinyl hydrogen) at τ = 4.0–4.7, a multiplet (terminal vinyl hydrogens) at τ = 4.9 to 5.3, a triplet (N–CH_2) at τ = 5.9 and a multiplet (3 methylenes) at τ = 7.9–8.7.

$C_{18}H_{19}N$ (249.34)	Calcd.	C 86.70	H 7.68	N 5.62
	Found	C 86.70	H 7.57	N 5.59

B. *Polymerization*

a) Materials

All solvents (BAKER analyzed reagents of PHILIPS pure grade) were refluxed and distilled from either sodium or calcium hydride. They were then stored over sodium wire in 4-l. standard-taper bottles from which they could be dispensed by means of nitrogen pressure.

Titanium tetrachloride (ANDERSON Chemical Co.) was used either as a 0.5 *M* solution in benzene, or as a 1 *M* solution in petroleum ether. α and γ titanium trichloride (STAUFFER Chemical Co.) were used without further purification as either a 0.8 *M* dispersions in benzene or as 1 *M* dispersions in petroleum ether. Vanadium trichloride (STAUFFER Chemical Co.) was used without further purification as a 1 *M* dispersion in petroleum ether. Aluminum alkyls (TEXAS ALKYLS Inc.) were used without purification as 20% solutions in heptane.

b) Polymerization method

Polymerizations were carried out either in bottles (A) or in small 3-necked flasks (B). Typical experimental procedures are as follows:

(A) *Bottle method*

Into a serum capped 100 ml. narrow neck bottle which had been previously baked for 1 hr. at 140 °C. and flushed with nitrogen for 1 hr., was placed by means of hypodermic syringes 30 ml. of solvent, 2 mmoles of $TiCl_3$, 5 mmoles of Et_2AlCl and 10 ml. of solvent containing 5.0 g. (0.02 mole) of 9-Δ^5-hexenylcarbazole. The bottle was then placed in a shaker bath at the desired temperature. At the conclusion of the reaction the bottle was vented with a hypodermic needle and 25 ml. of 10% anhydrous hydrogen chloride-methanol solution added to destroy the catalyst. The bottle was shaken for an additional 15 min., opened and the contents added to a large excess of methanol. The polymer was filtered and after repeated washings with fresh methanol dried in a vacuum oven at 40–50 °C. for 12 hrs.

(B) *3-Necked flask method*

In a 50 ml. 3-necked flask equipped with a reflux condenser, nitrogen inlet and a magnetic stirring bar was placed 0.004 mole of the monomer and 30 ml. of sodium-dried toluene. Moisture was rigorously excluded by flaming the entire apparatus prior to the introduction of monomer and oxygen was excluded by maintaining a blanket of purified nitrogen over the solution. To this stirred solution was added by means of hypodermic syringes 5 mmoles of Et_2AlCl and 2.5 mmoles of $TiCl_3$, in that order. At the termination of the reaction a few ml. of isopropanol was added to destroy the catalyst and the entire reaction mixture was added to a large excess of methanol. About 10 ml. of concentrated hydrochloric acid was then added and the polymer isolated by centrifugation. After repeated washing with fresh methanol the polymer was dried in a vacuum oven at 40–50 °C. for 12 hrs.

3. *Discussion*

Table 1 shows some of the catalyst systems and experimental conditions used in attempts to polymerize 9-Δ^3-butenylcarbazole. As can be seen, only one catalyst system was at all effective and only very low conversions could be achieved. Parallel attempts to polymerize 9-allylcarbazole were totally unsuccessful.

Table 1. The polymerization of 9-Δ^3-butenylcarbazole with Ziegler-Natta catalyst systems

No.	Catalyst system	Polymerization method	Ratio Al/Ti	Ratio monomer/Ti	Solvent	React. time (hrs.)	React. temp. (°C.)	Yield (%)
58	$TiCl_4$-Et_3Al	B	2.0	1.5	toluene	4	25	tr[a]
59	$TiCl_4$-Et_3Al	B	2.3	0.7	pet. ether	22	70	tr[a]
74-1	$\alpha TiCl_3$-Et_2AlCl	B	3.3	1.5	toluene	19	70	0
74-2	$\gamma TiCl_3$-$Al(iBu)_3$	B	1.0	4	*n*-heptane	18	25	0
85	$\gamma TiCl_3$-Et_2AlCl	B	1.4	1	toluene	19	70	2.5

[a] polyethylene.

The failure of 9-allylcarbazole and the extreme difficulty with which 9-Δ^3-butenylcarbazole polymerizes under these conditions is in sharp contrast with the behaviour of 9-vinylcarbazole, which under Ziegler-Natta catalysis easily yields polymers in high conversions[1,4]. Since in a previous paper[1] it was shown that 9-vinylcarbazole undergoes a facile cationic polymerization and that even weak Lewis acids such as $TiCl_3$ are very effective catalysts, this difference in behaviour indicates that 9-vinylcarbazole with Ziegler-Natta catalyst systems undergoes only a cationic polymerization. This easy cationic polymerization is, of course, due to the conjugation of the vinyl group and the carbazole ring. When this conjugation is prevented, as in 9-allylcarbazole or 9-Δ^3-butenylcarbazole, no cationic polymerization, even with strong Lewis acids such as $BF_3 \cdot Et_3O$ is observed.

Since Ziegler-Natta catalysis does not require a conjugation of a vinyl group with an electron donor system, it is reasonable to assume that if 9-vinylcarbazole polymerizes with these catalyst systems by a coordinate mechanism then 9-allylcarbazole and certainly 9-Δ^3-butenylcarbazole should also polymerize. The failure of these compounds to polymerize thus provides strong indirect evidence that 9-vinylcarbazole with Ziegler-Natta catalyst systems does not undergo a coordinate polymerization but merely undergoes a cationic polymerization.

These findings are not in accord with the work of SOLOMON, DIMONIE, AMBROZH and TOMESCU[4)], who studied the polymerization of 9-vinylcarbazole with a $TiCl_4$-nBuLi catalyst system and described a stereospecific polymerization yielding highly isotactic polymers having good crystallinity. On the basis of a kinetic study, these workers have also concluded that, with vinyl monomers having bulky heterocyclic substituents, steric hindrance did not take place, so that reaction rates comparable to vinyl aliphatic monomers are obtained.

In view of our present finding and our previously reported[1)] inability to repeat the stereospecific polymerization of 9-vinylcarbazole with a $TiCl_4$-nBuLi or any other ZIEGLER-NATTA catalyst system, it is believed that the conclusions of SOLOMON, DIMONIE, AMBROZH and TOMESCU regarding the lack of steric hindrance in the ZIEGLER-NATTA polymerization of 9-vinylcarbazole are in error and that, if any stereospecificity was indeed observed, it was not due to a ZIEGLER-NATTA catalysis, but rather to a cationic catalysis.

Recent work[5)] repeated in these laboratories[6)] has shown that 9-vinylcarbazole can be polymerized at $-78\,°C$. using cationic catalysis such as $EtAlCl_2$ and that polymers reported[5)] to have a crystallinity of 35–50% can be prepared. However, it is considered very unlikely that under the polymerization conditions utilized by SOLOMON, DIMONIE, AMBROZH and TOMESCU a similar stereoregulated polymerization of 9-vinylcarbazole took place.

The fact that ZIEGLER-NATTA catalysts are totally ineffective with 9-allylcarbazole and only very slightly effective with 9-Δ^3-butenylcarbazole suggests that, aside from complexing difficulties which might arise from the nitrogen atom in the heterocyclic carbazole nucleus, steric hindrance about the double bond plays a very important part in determining the reactivity of these monomers.

The effect of steric hindrances about a vinyl group has been investigated by NATTA, DANUSSO and SIANESI[7,8)], who have studied the stereospecific polymerization of a number of vinyl aromatic monomers and have concluded that the nature and number of substituents not only affects the crystallinity of the polymer, but also has a strong influence on the reactivity of the monomer. Of particular interest was the fact that 9-vinylanthracene, which shows similar steric hindrance about the vinyl group as 9-vinylcarbazole, could not be polymerized with a ZIEGLER catalyst system. A recent report does claim a ZIEGLER polymerization of 9-vinylanthracene with a $TiCl_4$–$AlEt_3$ catalyst system[9)]. However, the data appear to be more consistent with a predominantly cationic polymerization, since $TiCl_4$ alone readily polymerized 9-vinylanthracene and the yield of polymer increased from 20 to 90% as the Al/Ti ratio was decreased from 4 to 2.

NATTA, DANUSSO and SIANESI[7,8] have also shown that with substituted styrenes monomer reactivity is sharply inhibited by ortho monosubstitution and is completely inhibited by ortho disubstitution. Similar results were also obtained by OVERBERGER and NOZAKURA[10], who were not able to polymerize or copolymerize 2,6-dimethylstyrene with a $TiCl_3-Al(iBu)_3$ catalyst system. Thus, it is clear that the polymerization process is very sensitive to the presence of hindering substituents in the proximity of the vinyl group.

Although the failure of 9-allylcarbazole to polymerize and the extremely poor conversion which is realized with 9-Δ^3-butenylcarbazole is most likely due to a steric hindrance factor, the possibility that the basic nitrogen atom in the heterocyclic carbazole forms an irreversible complex with the active catalyst sites must also be considered. It thus became of interest to study the polymerization of the two next higher homologues, 9-Δ^4-pentenylcarbazole and 9-Δ^5-hexenylcarbazole, where by eliminating most of the steric hindrance factors any complexing action of the carbazole nitrogen might become apparent.

Table 2. The polymerization of 9-Δ^4-pentenylcarbazole with ZIEGLER-NATTA catalyst systems

No.	Catalyst system	Polymerization method	Ratio Al/Ti or V	Ratio monomer/Ti or V	Solvent	React. time (hrs)	React. temp. (°C.)	Yield (%)	Inh.*) visc
94-2	$\gamma TiCl_3-Et_2AlCl$	B	2.0	1.6	toluene	19	70	36.5	0.07
S-71	$\gamma TiCl_3-Et_2AlCl$	A	2.5	10	benzene	72	50	53	0.22
S-60	$\gamma TiCl_3-Et_2AlCl$	A	2.5	100	benzene	72	50	7.5	0.36
94-1	$\gamma TiCl_3-Et_3Al$	B	2.0	1.6	toluene	19	70	13	–
94-3	VCl_3-Et_2AlCl	B	2.0	1.6	toluene	19	70	2	–
99-2	$\alpha TiCl_3-Et_2AlCl$	B	2.0	1.6	toluene	21	70	2.6	–
99-3	$\gamma TiCl_3-Al(iBu)_3$	B	2.0	1.6	toluene	21	70	9.2	–

*) N-methylpyrrolidone at 123 °C. (0.250 g./100 ml.).

Results of polymerization studies with these two compounds are shown in Table 2 and Table 3. As can be seen, most of the usual ZIEGLER-NATTA catalyst systems lead to some polymer formation, but only one system, the $\gamma TiCl_3-Et_2AlCl$, gives reasonable yields. It is interesting to note that the substitution of $\alpha TiCl_3$ for $\gamma TiCl_3$ leads to a substantial decrease

Table 3. The polymerization of 9-Δ^5-hexenylcarbazole with Ziegler-Natta catalyst systems

No.	Catalyst system	Polymerization method	Ratio Al/Ti or V	Ratio monomer/Ti or V	Solvent	React. time (hrs.)	React. temp. (°C.)	Yield (%)	Inh.*) visc.
91-2	$\gamma TiCl_3$-Et_2AlCl	B	2.0	1.6	toluene	10	70	49	0.07
S-72	$\gamma TiCl_3$-Et_2AlCl	A	2.5	10	benzene	72	50	50	0.19
S-69	$\gamma TiCl_3$-Et_2AlCl	A	2.5	10	benzene	72	70	30	0.20
S-70	$\gamma TiCl_3$-Et_2AlCl	A	2.5	100	benzene	72	70	30	0.42
99-1	$\alpha TiCl_3$-Et_2AlCl	B	2.0	1.6	toluene	21	70	4.8	–
84-B	$\gamma TiCl_3$-Et_3Al	B	1.4	1.2	toluene	20	70	tr.	–
83-B	$\gamma TiCl_3$-$Al(iBu)_3$	B	1.4	1.2	toluene	17	70	18	0.08
80	$\alpha TiCl_3$-$Al(iBu)_3$	B	1.4	1.2	toluene	19	70	tr.	–
82	VCl_3-$Al(iBu)_3$	B	1.4	1.2	toluene	21	70	5	0.20
88-1	VCl_3-Et_2AlCl	B	2.0	1.6	toluene	20	70	8	0.42

*) N-methylpyrrolidone at 123 °C. (0.250 g./100 ml.).

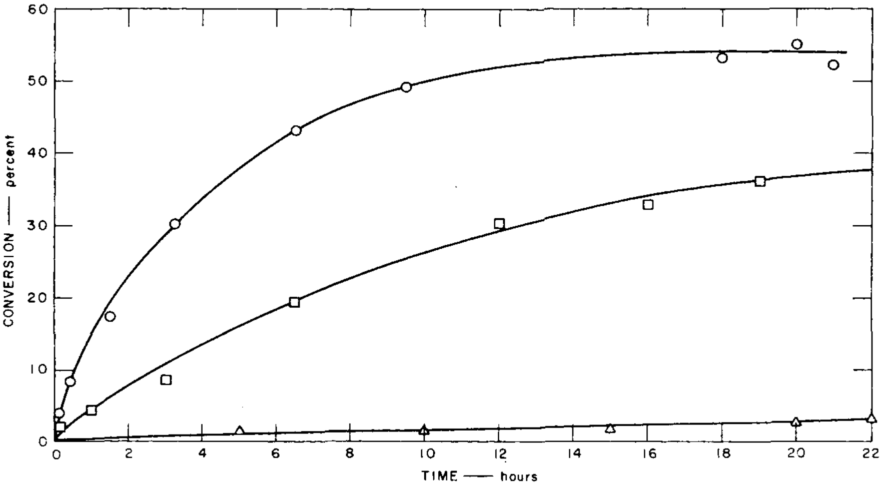

Fig. 1. Conversions of monomers as a function of time for (△) 9-Δ^3-butenylcarbazole, (□) 9-Δ^4-pentenylcarbazole and (○) 9-Δ^5-hexenylcarbazole in toluene at 70 °C. Monomer concentration 0.133 mole/l.; catalyst = Et_2AlCl-$\gamma TiCl_3$; Al/Ti = 2; $\gamma TiCl_3$/monomer = 0.625.

in polymer yield, under otherwise similar experimental conditions. Similarly, the substitution of Et_3Al for Et_2AlCl also results in a great decrease in conversion. Of further interest is the fact that, while for a titanium-aluminum system the inherent viscosities at a relatively low monomer/

catalyst ratio are rather low, this is not true for a vanadium-aluminum catalyst system.

A comparison of the reactivities with a $\gamma TiCl_3-Et_2AlCl$ catalyst system for all 3 monomers is shown in Fig. 1, where the percent conversion has been plotted as a function of the reaction time. It will be noted that the initial polymerization rate of 9-Δ^5-hexenylcarbazole is somewhat greater than that of 9-Δ^4-pentenylcarbazole and that it reaches its limiting value of about 55 percent considerably sooner. Both monomers, however, after a long reaction time, approach the same limiting conversion.

In a recent paper DUNHAM, VANDENBERGHE, FABER and CONTOIS[11) have described the polymerization and properties of a number of olefins having the general formula $CH_2{=}CH(CH_2)_xR$, where x = 0–3 and R is methyl, isopropyl, *tert*-butyl, phenyl, or cyclohexyl. It was interesting to note that in all cases except where R was *tert*-butyl high conversions to polymer were realized. However, with R = *tert*-butyl, only trace amounts of polymer were isolated when x was 0, 1 or 2. With x = 3 a 57 % conversion was obtained after 16 hrs. at 50 °C. These results are in remarkably good agreement with the present work and seem to suggest that the steric effect of a carbazole nucleus on the polymerization rate is about the same as that of a *tert*-butyl group thus indicating the absence of any detrimental complexing due to the carbazole nitrogen.

Table 4. Physical properties and fractionation of poly(9-Δ^4-pentenylcarbazole) and poly (9-Δ^5-hexenylcarbazole). For experimental conditions see Table 2 and Table 3

No.	Polymer	Ratio Monomer/Ti	Inh.**) visc.	Acetone insoluble		
				%	PMT*)	Inh.**).visc
94-2	pentenyl	1.6	0.07	52	142	—
S-71	pentenyl	10	0.22	74	142	0.23
S-60	pentenyl	100	0.36	89	137	0.39
91-2	hexenyl	1.6	0.07	47	115	0.08
S-69	hexenyl	10	0.20	73	120	0.26
S-70	hexenyl	100	0.42	82	114	0.45

*) Polymer Melt Temperature defined as that temperature at which the polymer leaves a molten trail when stroked across a heated brass surface using moderate pressure.

**) N-methylpyrrolidone at 123°C. (0.250 g./100 ml.).

In Table 4 are shown extraction data, polymer melt temperatures and inherent viscosities for some polymers of 9-Δ^4-pentenylcarbazole and 9-Δ^5-hexenylcarbazole. It will be noted that in both series the inherent viscosity increases as the ratio of monomer to catalyst increases. It will also be noted that the percent acetone insoluble fraction increases sharply with increasing inherent viscosity. In each case, the inherent viscosity of the acetone insoluble fraction was somewhat higher than that of the original polymer, indicating that the extraction procedure removed some low molecular weight material. It is, of course, also possible that the acetone extraction procedure removed some nonstereospecific product. However, no differences were apparent in the infrared spectra of soluble and insoluble products and thus no correlated between acetone insolubility and stereospecificity could be made.

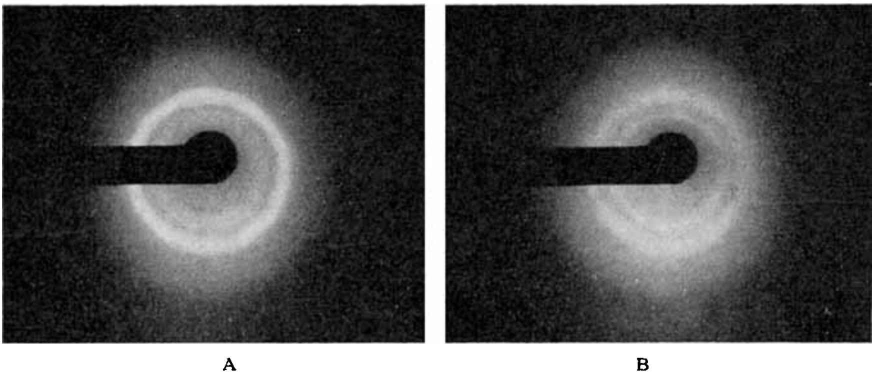

Fig. 2. X-ray diffraction patterns (Cu-Kα, Ni-filtered) of (A) poly(9-Δ^4-pentenylcarbazole) – sample S-60, acetone insoluble and (B) poly(9-Δ^5-hexenylcarbazole) – sample S-70, acetone insoluble

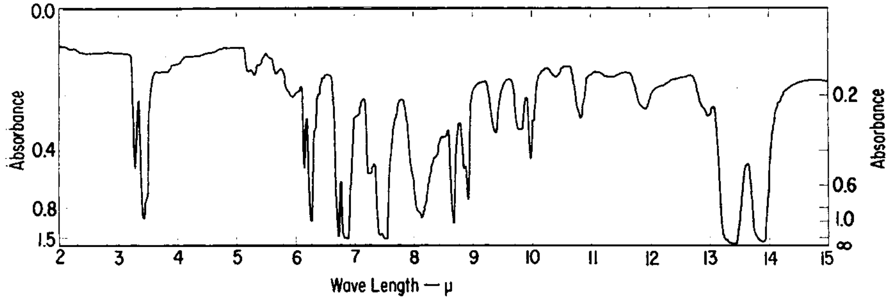

Fig. 3. Infrared spectrum of poly(9-Δ^4-pentenylcarbazole)

Fig. 2 shows X-ray diffraction patterns of a poly(9-Δ^4-pentenylcarbazole) and a poly(9-Δ^5-hexenylcarbazole) sample. Although the X-ray diffraction pattern is not characteristic of a highly crystalline polymer, it does, however, indicate a considerable degree of steric order. Indeed, considering the large size of the carbazole nucleus, the sharpness of the lines noted in the diffraction pattern could very well be indicative of a very high crystallinity. A high degree of crystallinity is also indicated by the insolubility of the polymers in most organic solvents.

The infrared spectrum of poly(9-Δ^4-pentenylcarbazole) is shown in Fig. 3. Except for the expected difference in the ratio of aromatic C–H ($3.28\,\mu$) to aliphatic C–H ($3.43\,\mu$) stretching frequency intensities, the infrared spectra of all three polymers were virtually identical.

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