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Received on 11.12.2006

UDC 547.759.32+678.02

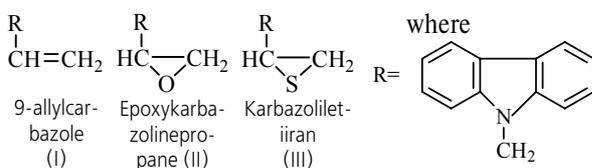
POLYMERIZATION OF 9-ALLYLCARBAZOLE, EPOXYKARBAZOLYLPROPANE AND KARBAZOLYLTIIRAN

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The ability to 9-allylcarbazole polymerization both with radical type activators and ion catalysts has been shown. The conditions were found and polymerization techniques of 9-allylcarbazole, 9-karbazolyliiran and 9-epoxykarbazolypropene were suggested.

9-allylcarbazole (9AC, I) is formed practically with quantitative output at interaction of carbazole with allyl halogenides with caustics in the medium of dipolar aprotic solvents and may be easily refined from impurities by recrystallization from isopropyl alcohol [1].



Structural analog of 9-allylcarbazole (I) – 9-vinylcarbazole (9VC) – is widely known owing to its polymer – polyvinylcarbazole (PVC) – the best one among organic semiconductors found wide application in nonsilver processes of recording, storing and multiplication of information. Polymerization of 9AC in comparison with 9VC is not practically studied. In short reports about the possibility of 9AC polymerization [2, 3] there was no information on conditions of process carrying out and polymer properties. It is known from scientific literature sources that allylic monomers may be polymerized by radical and ion mechanisms [4, 5]. Therefore 9AC polymerization with activator of both radical and ion type

was studied. Polymerization of epoxykarbazolypropene (EKP, II) and epiteokarbazolpropan (karbazolyltiiran – KT, III) as possible comonomers in polymerization processes of their copolymerization with 9AC was studied parallel. Polymerization completeness was controlled by the method of thin-layer chromatography (TLC: sorbent – syluphol, eluent – benzene).

It was stated experimentally that radical polymerization of 9AC at temperature change from 60 to 100 °C and concentration of radical polymerization initiator of dinitrile azobisisooil acid (DAA) from 0,1 to 30 % from mass of loaded monomer polymerization does not occur. It is probably explained by low activity of allylic radicals in polymerization processes [5]. At temperature increase up to 100 °C the rate of polymerization rises. However parallel with formation of 9AC polymer (polyallylcarbazole, PAC) the side reactions attended by formation of karbozalylacetic acid and dikarbozalylpropanol occur. Presence of these substances was stated by the method of TLC using taps of the given substances.

EKP and KT polymerization at temperature 110 °C and addition of 30 % DAA or benzoil peroxide (BP) to monomer weight also occur. To confirm initiator participation in formation of polyepoxykarbazolypropene

(PEKP) and polykarbazoliletiiran (PKT) thermal polymerization of EKP and KT was carried out. It was shown with the help of TLC that without DAA and BP polymerization of EKP and KT at heating to 110 °C during 32 h does not occur. Conditions and results of radical polymerization of 9AC, EKP and KT are given in Table 1.

Table 1. Conditions and results of radical polymerization of monomers at 110 °C

Monomer	Monomer load, g	Initiator, wt. %	Solvent, toluene, ml	Duration, h	Yield, wt. %
9AC	1,0	DAA, 15	–	26	0,9
	0,2	DAA, 30	–	26	5,0
	0,2	BP, 30	0,35	26	30,0
	1,0	DAA, 30	0,35	26	20,0
	0,2	BP, 30	0,35	26	19,5
	2,0	DAA, 30	1,0	32	17,3
EKP	0,2	DAA, 30	–	26	40,0
	0,2	BP, 30	0,35	26	17,0
	0,2	DAA, 30	0,35	26	16,0
	2,0	BP, 30	1,0	32	14,0
KT	0,2	DAA, 30	–	26	13,3
	0,2	BP, 30	0,35	26	15,1
	0,2	DAA, 30	–	26	13,6
	0,2	BP, 30	0,35	26	14,1
	2,0	BP, 30	1,0	32	33,6

Results of experiments of Table 1 indicate rather slow course of polymerization processes of studied monomers and require rather hard conditions (high concentration of initiators, temperature and duration). Output of polymers refined by oversedimentation from toluene to hexane does not exceed 30 K 40 wt. %. Polymerization in toluene medium homogenizing reactionary medium affects favorably. However solvent content should not be increased. At polymerization of 9AC and KT BP is more efficient as an activator and at EKP polymerization DAA and bulk polymerization are more preferable.

AlCl_3 , HClO_4 , $\text{Mg}(\text{ClO}_4)_2$, SnCl_4 , $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_2\text{AlCl}$ were tested as catalysts of ion type. Experiments were carried out by the following technique. Monomer is loaded into test tubes of heat-resistant glass with thoroughly ground corks; preliminary drained toluene is poured (or other solvent if the presence of solvent is stipulated by polymerization condition). Reactionary mass is kept till complete monomer dissolution and after that catalyst is added and test tubes are pressurized. Polymerization is carried out at constant temperature maintained with accuracy to 1 °C to complete monomer conversion. Completeness of conversion is controlled by the method of TLC.

Original 9AC, EKP and KT are obtained by known methods [1, 6, 7] respectively and represent pure individual substances. The rest used agents had qualification «pure» or «AR» (for example, for TLC). At the end of polymerization the reaction mass contains as a rule insoluble fraction in the form of sediment along with solution. Sediment is filtered at Chott filter and polymer is extracted from manifold by precipitation from toluene solution into hexane. If it is necessary oversedimentation is repeated to complete absence of impurities in polymer (control – TLC).

It was stated experimentally that polymerization of 9AC as well as EKP and KT with AlCl_3 monomer bulk does not practically occur. Addition of water trace concentrations as cocatalysts did not accelerate the process. In toluene medium at 20 °C and duration of polymerization 32 h polymers 9AC (PAC) and EKP (PEKP) were obtained with output 1 %, and polymer KT (PKT) – with output 25,5 %. At temperature rise up to 80 °C polymerization rate of all monomers increases significantly. However, all obtained polymers are high-melting and sparingly soluble and therefore using AlCl_3 as a catalyst is hardly reasonable

HClO_4 and $\text{Mg}(\text{ClO}_4)_2$ do not practically initiate polymerization process of 9AC, EKP and KT both at 20 °C and being heated to 60 °C. Addition of cocatalyst (H_2O) does not change the picture of the process.

As for SnCl_4 use as a catalyst then bulk polymerization both at 20 °C and at temperature increase up to 80 °C and catalyst concentration 0,1 % is inappropriate for any monomers. It is explained first of all by difficulty of catalyst distribution in monomer mass. In dioxane medium at 20 °C and concentration SnCl_4 0,1 % to monomer mass the polymerization does not practically occur and at heating to 60 °C and SnCl_4 0,5% content to monomer mass PAC with output 39 % is obtained. In toluene medium at 20 °C even at catalyst content of 30 wt. % 9AC, EKP and KT are slowly polymerized and yield of PAC, PEKP and PKT amounted to 20, 15 and 11 %, respectively at polymerization duration 32 h. Polymerization of 9AC, EKP and KT in toluene at 80 °C and content of SnCl_4 30 wt. % allows obtaining their polymers with rather high output and brining polymerization processes to complete monomer consumption (TLC data).

$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (etherate of trifluoro boron or ETFB) and $(\text{C}_2\text{H}_5)_2\text{AlCl}$ (diethylaluminumchloride or DEACH) possess the highest activity in the studied catalyst series. It was shown that at room temperature with 0,1 K 0,5 wt. % ETFB of 9AC is not polymerized. 9AC, EKP and KT in toluene medium at 80 °C and catalyst content of 30 wt. % are polymerized to complete monomer consumption and PAC, PEKP and PKT are obtained with output 80, 100 and 90 % respectively. 9AC, EKP and KT are also polymerized with DEACH to complete monomer consumption and with high polymer output. Conditions and results of 9AC, EKP and KT polymerization with ion catalysts are given in Table 2.

The obtained results allow making conclusion about appropriateness of 9AC, EKP and KT polymerization in toluene medium and with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (etherate of trifluoro boron) at 80 °C and $(\text{C}_2\text{H}_5)_2\text{AlCl}$ (diethylaluminumchloride) at 70 °C.

Polymers of PAC, PEKP and PKT obtained with SnCl_4 have intensive dark blue color connected probably with complex formation. Polymers are poorly dissolved in most part of organic solvents, have high softening points. Polymer films obtained with SnCl_4 (cloudy, of low quality) are hardly of great interest in nonsilver processes of information recording. All polymers obtained with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and $(\text{C}_2\text{H}_5)_2\text{AlCl}$ refined by oversedimentation

tion from toluene to hexane dissolve in organic solvents and form from solutions transparent films possessing good adhesion to aluminum, glass, brass as well as oil-, petroleum- and water resistance. Properties of polymers obtained at ionic polymerization are given in table 3.

Table 2. Conditions and results of ion polymer polymerization with different catalysts

Monomer	Monomer load, g	Initiator, wt. %	Solvent, ml	Temperature °C	Duration, h	Yield, wt. %
AC	1	SnCl ₄ ; 0,5	Dioxane, 5	60	5	39
	1	BF ₃ ·O(C ₂ H ₅) ₂ ; 0,5	Dioxane, 5	60	5	10
	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	20	32	4
	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	80	32	9
	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 2	80	32	80
	0,2	AlCl ₃ ; 30	Toluene, 1	20	32	1
	0,2	AlCl ₃ ; 30	Toluene, 1	80	32	25
	0,2	SnCl ₄ ; 30	Toluene, 1	20	32	20
	0,2	SnCl ₄ ; 30	Toluene, 1	80	32	98
	2,0	SnCl ₄ ; 30	Toluene, 2	80	32	68
	0,2	(C ₂ H ₅) ₂ AlCl; 5·10 ⁻³	Toluene, 1	70	32	52
	0,2	(C ₂ H ₅) ₂ AlCl; 1·10 ⁻²	Toluene, 1	70	31	19
	0,2	(C ₂ H ₅) ₂ AlCl; 2·10 ⁻²	Toluene, 1	70	14	90
	EKP	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	20	32
0,2		BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	80	32	29
2,0		BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 2	80	32	100
0,2		AlCl ₃ ; 30	Toluene, 1	20	32	1
0,2		AlCl ₃ ; 30	Toluene, 1	90	32	36
0,2		SnCl ₄ ; 30	Toluene, 1	20	32	1,5
0,2		SnCl ₄ ; 30	Toluene, 1	80	32	42
2,0		SnCl ₄ ; 30	Toluene, 2	80	32	68
0,2		(C ₂ H ₅) ₂ AlCl; 5·10 ⁻³	Toluene, 1	70	32	35
0,2		(C ₂ H ₅) ₂ AlCl; 1·10 ⁻²	Toluene, 1	70	32	50
KT	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	20	32	15
	0,2	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 1	80	32	33
	2,0	BF ₃ ·O(C ₂ H ₅) ₂ ; 30	Toluene, 2	80	32	90
	0,2	AlCl ₃ ; 30	Toluene, 1	20	32	25
	0,2	AlCl ₃ ; 30	Toluene, 1	80	32	40
	0,2	SnCl ₄ ; 30	Toluene, 1	20	32	11
	0,2	SnCl ₄ ; 30	Toluene, 1	80	32	62
	2,0	SnCl ₄ ; 30	Toluene, 2	80	32	59
	0,2	(C ₂ H ₅) ₂ AlCl; 5·10 ⁻³	Toluene, 1	70	32	97
	0,2	(C ₂ H ₅) ₂ AlCl; 1·10 ⁻²	Toluene, 1	70	31	41
0,2	(C ₂ H ₅) ₂ AlCl; 2·10 ⁻²	Toluene, 1	70	14	35	

Note: (C₂H₅)₂AlCl concentration is given in mole/l

Structure of the obtained polymers is confirmed by IR-spectra (UR-20, film) [8, 9]. IR-spectra of PAC, PEKP and PKT contain bands typical for oscillation of CH-bonds in nonsubstituted carbazole ring with maximum absorption at 760 and 720 cm⁻¹; bands typical for oscillation of carbazole fragment with maximum absorption 1610 and 1496 cm⁻¹, as well as absorption bands at 1340 K1330 cm⁻¹, indicating presence of C-N bond. Band disappearance in the range of 820 and 1620 cm⁻¹

in PAC spectrum typical for end-CH=CH₂ bond and presenting in spectrum of monomer 9AC indicate PAC formation by double bond opening. Disappearance in IR-spectrum of PEKP bands in the range of 918, 1165 and 1265 cm⁻¹ typical for valence oscillations of C-O bond of epoxy ring and presenting in monomer EKP spectrum indicate the formation of polyepoxykarbazolylpropan chain by opening epoxy ring.

Table 3. Properties of polymers obtained at ion polymerization

Polymer sample	Catalyst	Softening point, °C	Molecular weight	Chemical stability of films, %					Photosensitive properties		
				Oil-	Petroleum-	Water-	Acid-	Alkali-	Charge potential, B	Light charge half-decay, s	Photosensitivity J/(cm ²)
PAC	SnCl ₄	140...166	5100	98	98	98	10	1	60	77	55,3
PEKP	SnCl ₄	152...182	-	97	99	99	0	1	-	-	-
PKT	SnCl ₄	163...171	3900	96	96	85	2	2	40	180	23,5
PAC	BF ₃ ·O(C ₂ H ₅) ₂	152...173	4200	78	40	65	12	20	25	63	67,6
PEKP	BF ₃ ·O(C ₂ H ₅) ₂	168...180	3000	82	68	64	10	22	50	101	42,2
PKT	BF ₃ ·O(C ₂ H ₅) ₂	172...188	3100	42	67	70	10	10	75	38	112,1
PAC	(C ₂ H ₅) ₂ AlCl	163...179	-	96	84	70	21	13	60	70	60,8
PEKP	(C ₂ H ₅) ₂ AlCl	217...233	5200	80	52	92	18	9	50	145	29,4
PKT	(C ₂ H ₅) ₂ AlCl	171...213	3600	87	90	28	34	20	85	30	141,0

Presence in IR-spectrum of PKT band in the range of 650 cm⁻¹ typical for oscillation of C-S bond and band in the range of 2550 cm⁻¹ typical for S-H bond, confirm opening of tiiran cycle at KT polymerization.

Polymers obtained with initiators of radical type represent solid white substances with low molecular weight and low softening points: PAC (initiator DAA) 71 K 110 °C; PEKP (initiator BP) 65 K 113 °C; PKT (initiator BP) 57 K 108 °C. All oligomers are soluble in organic solvents and form transparent flexible films by irrigation from solutions.

Oligomers obtained with ion type activators are more high-melting and harder to be dissolved. It was stated that BF₃·O(C₂H₅)₂ is more active catalyst and in its presence the rate of 9AC polymerization is comparable with KT and EKP. However, polymers obtained with (C₂H₅)₂AlCl are more flexible and dissolve easily.

Chemical stability was estimated by film adhesion changing after their hold in water, mineral oil, petroleum, 20 % sulfuric acid and 20 % solution of caustic soda at 20 °C during 24 h. Adhesion was cross-cut tested by SS 15140-78.

Polymer molecular weight was determined by cryoscopic method by [10].

To determine photosensitive polymer properties the polished and fat-free brass substrates are coated with films by the method of irrigation from solution; they are dried at 20 °C during 24 h and after that are charged with corona discharge. Charge potential is measured, time of primary potential half-decay is fixed at lightning with polychromic light, and photosensitivity is computed [11].

The results of film photosensitive properties defining should be considered as searching (preliminary). Special researches are required for working-off film preparation technologies from ready polymers. The preliminary results indicate the ability of polymer films to be charged in corona discharge and charge runoff at light-

ning that is about polymer fitness for obtaining materials with photosensitive properties.

The obtained results do not allow explaining the detailed mechanism of the processes but do not contradict scientific data about the given process history [2–5].

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Received on 26.09.2007