Polymer Bulletin 26, 193–198 (1991)

Polymer Bulletin

Heats of polymerization of carbazolyl-substituted epoxides

Pranas Brūzga, Juozas Gražulevičius*, Rimtautas Kavaliūnas, and Rimantas Kublickas

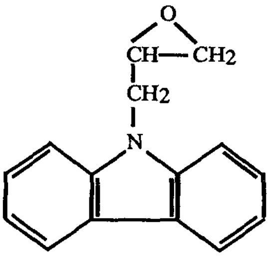
Department of Organic Technology, Kaunas Technological University, Radvilenų Plentas 19,
233028 Kaunas, Lithuania

Summary

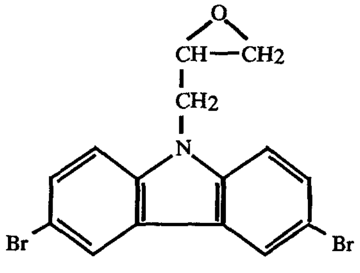
Heats of polymerization of three carbazolyl-containing epoxides 9-(2,3-epoxypropyl)carbazole, 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane and 3,6-dibromo-9-(2,3-epoxypropyl)carbazole have been determined on the differential microcalorimeter DAK 1-1A (USSR). The influence of the structure of monomers upon the values of polymerization heat is discussed.

Introduction

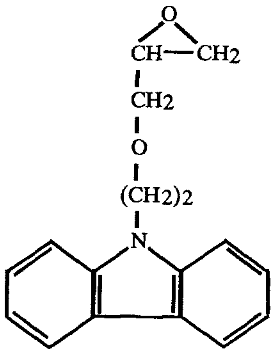
Carbazolyl-substituted polyethers are widely used as organic photoconductors in electrophotography and in some other fields of silverless photography (1-3). The most important representatives of such photoconductive polyethers are oligomers and polymers of 9-(2,3- epoxypropyl)carbazole (EPC), 3,6-dibromo-9-(2,3-epoxypropyl)carbazole (DBEPC) and 1,2-epoxy-6-9-(carbazolyl)-4-oxahexane (ECOH), which are synthesized by ionic polymerization of the corresponding epoxy monomers:



EPC



DBEPC



ECOH

Polymerization reactions are usually accompanied by a considerable heat effect. However, search of the chemical literature has revealed no values for the heat of polymerization of more complex than ethylene oxide, propylene oxide, styrene oxide epoxy monomers (4,5). The reliable values for the heat of polymerization are indispensible for the transformation of differential heat flow rate curves into conversion versus time curves (kinetic curves of polymerization) if polymerization is studied by the microcalorimetric technique. This method is almost irreplacable for the investigation of oligomerization of carbazolyl-substituted epoxides since other continues methods like dilatometry are not enought sensitive. On the other hand some of the above mentioned photoconductive polymers are produced

---

*To whom offprint requests should be sent on the industrial scale or are prepared for such production, so the data concerning heats of polymerization are necessary for the designing of the thermal regime of reactors.

Experimental

Materials

EPC (from " Biolar ", Latvia) was recrystallized twice from ethyl alcohol (mp 110-111° C). ECOH was synthesized by condensation of 9-(2-oxyethyl)carbazole with epychlorohydrin in the presence of KOH (6). It was purified by recrystallization from ethyl alcohol (mp 57.5-58°C). DBEPC was obtained by bromination of EPC with N-bromosuccinimide (7) . It was recrystallized from toluen (mp 141-142° C). 9-vinylcarbazole (from " Reakhim ", USSR) was recrystallized from ethanol and hexane (mp 64.5-66° C).

For the determination of heat of polymerization EPC was polymerized with tertiary amines - dimethylcyclohexylamine (DMCHA), and dimethylbenzilamine (DMBA), ECOH was polymerized with triphenylcarbenium salts in 1,2-dichloroethane, 9-vinylcarbazole was polymerized with 2,4,6-triphenylpyrilium perchlorate. DMCHA and DMBA (Fluka AH) as well as triphenylcarbenium salts - triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$), triphenylcarbenium hexachloroantimonate ($Ph_3C^+SbCl_4^-$) and triphenylcarbenium pentachlorostannate ($Ph_3C^+SnCl_5^-$) (all from Aldrich) were used as received. 1,2-dichloroethane was purified by conventional procedure (8).

Polymerization

Polymerization of EPC and ECOH with tertiary amines was carried out in the nitrogen blanket. Polymerization of DBEPC with triphenylcarbenium salts was carried out in dichloroethane in the air equilibrated atmosphere. Polymerization initiated with tertiary amines was stopped by the sudden cooling of the reaction mixture to the solid state. Polymerization of DBEPC was stopped by the dilution of the reaction mixture with dimethylformamide which is known as inhibitor of cationic polymerization.

The average degree of polymerization of the obtained carbazolyl-containing oligoethers was 4-5.

Measurements

Differential automatic microcalorimeter DAK 1-1 A (from Chernogolovka, USSR) was used for the recording of (heat flow rate) versus time curves under the isothermal conditions. A special long glass tube was designed for DAK 1-1 A for the introduction of the samples into the measuring block. A " floating " glass stick fitted into the tube via the hydraulic back-pressure valve was used for breaking a capsule containing initiator or its solution. The wall thickness of initiator capsules was carefully chosen. These capsules should be strong enough to withstand the weight of the braker but at the same time they should be easily broken subsequently to initiate polymerization. The height of the capsule has to be chosen so that the whole capsule would be covered by the monomer melt or solution. Total heat of the reaction was estimated by integration of area under the curve expressing the (heat flow rate) versus time function. Thermal energy generated by the breaking of the capsule and by homogenization of the reaction mixture in case of polymerizatrion of EPC and ECOH with tertiary amines was eliminated graphically. In case of cationic polymerization of DBEPC because of high initial heat flow rate these heat by-effects were eliminated mathemathycally. The value of heat of polymerization of the title monomers was established from the relation of the total thermal energy of the reaction and the number of moles of the converted monomer. Monomer conversion was determined by GPC from the relation of integral area under the elution curve of oligomer and that under the curve of (oligomer plus monomer). A column packed with " Sephadex LH-20 " was used for GPC analysis using dimethylformamide as eluent.

IR-spectra of monomers and oligomers were recorded on UR-20 spectrophotometer (Carl Zeiss, Jena).

Results and discussion

IR spectroscopy and GPC analysis of oligomers and of the corresponding monomers have revealed no side reactions in the investigated systems. Consequently, only reaction of polymerization which goes on via opening of epoxy ring and formation of ether bonds determins the heat effects of those reactions.

According to Calvet (9) the total heat effect of the chemical process is equal to the algebraic sum of heat effects of the constituent stages of the process. The total heat effect of the reaction of polymerization of EPC and ECOH in bulk with tertiary amines can be presented as the sum of three constituent heat effects:

$$Q = Q_1 + Q_2 + Q_3 ,$$

where Q_1 is heat of solution of tertiary amine in monomer, Q_2 is heat of polymerization and Q_3 is heat effect of mixing of oligomer and monomer. For the establishment of Q_3 series of experiments on the estimation of the heat effect of mixing of EPC and the corresponding oligomer poly[9-(2,3-epoxypropyl)carbazole] were carried out at different ratio of the components. The solution heat of tertiary amine in EPC and ECOH was estimated in the presence of the small amount of the solvent - chlorobenzene which dramatically decreased the initial rate of polymerization and enabled to separate graphically on the differential heat flow rate curve the peak corresponding to the heat effect of the mixing (Q_1) from the peak corresponding to the heat effect of polymerization. It was established that the sum $Q_1 + Q_3$ does not exceed 0.5 % from Q_2, therefore the values Q_1 and Q_3 were neglected in calculations of polymerization heat. On the similar grounds heat effects of the side processes were neglected in case of polymerization of DBEPC in 1,2 - dichloroethane with triphenylcarbenium salts. The heat effects of formation of end groups which should be rather considerable in the reaction of oligomerization in our work is reflected in the value of heat effect of the main reaction. Such reflection is reasonable mainly all from the point of view of the practical use of the thermodinamic data.

In order to establish polymerization heat of EPC 10 polymerizations at 120, 130, 140° C were carried out with different amounts of DMBA and DMCHA. The data obtained are presented in Table 1.

It is evident from Table 1 that heat of polymerization of EPC does not depend on the catalyst used or its concentration. In contrast to the data conserning carbazole-substituted vinyl monomers (10) no dependance of heat of polymerization on temperature of reaction has been observed. The averaraged values of heat of polymerization of EPC is:

$$-\Delta H = 99.09 \pm 1.76 \text{ kJ / mole}$$

Table 1. Heat of Polymerization (-ΔH) of EPC

Sample of EPC, g	Catalyst	Weight of catalyst, g	Temperature, °C	Conversion of EPC	Q, J	-ΔH, kJ / mole
0.10570	DMBA	0.02240	120	0.950	43.190	96.03
0.10495	DMBA	0.01165	120	0.956	45.088	100.30
0.09620	DMCHA	0.01010	120	0.941	39.470	97.33
0.10000	DMCHA	0.00150	120	0.956	42.910	100.21
0.10235	DMCHA	0.00150	120	0.953	42.531	97.35
0.10000	DMCHA	0.00410	120	0.952	43.372	101.71
0.09985	DMCHA	0.00415	130	0.890	39.500	99.24
0.10010	DMCHA	0.00200	130	0.953	42.359	99.14
0.09990	DMCHA	0.00295	130	0.908	40.712	100.17
0.10005	DMCHA	0.00415	140	0.948	42.260	99.45

For the estimation of polymerization heat of ECOH 10 polymerizations were carried out in the comparatively wide range of temperatures (at 70, 100 and 120° C) with different amounts of DMCHA. The data obtained are presented in Table 2.

Table 2. Heat of Polymerization of ECOH

Sample of ECOH, g	Weight of catalyst, g	Temperature, ° C	Conversion of ECOH	Q, J	-ΔH, kJ / mole
0.10200	0.00405	70	0.977	35.865	96.19
0.10190	0.00420	70	0.976	35.298	94.88
0.10050	0.00840	70	0.918	34.340	99.50
0.09945	0.00880	70	0.987	35.009	95.37
0.10200	0.00225	70	0.982	35.831	95.63
0.09990	0.00420	100	0.954	33.504	93.98
0.10045	0.00840	100	0.973	36.268	98.32
0.10020	0.00860	120	0.968	34.987	96.41
0.10085	0.00220	120	0.889	32.618	97.30
0.10230	0.00410	120	0.962	34.695	94.25

Despite wide range of temperatures at which heat of polymerization was estimated no dependance of its value upon temperature was observed for ECOH. The averaged value of heat of polymerization of ECOH is:

$$-\Delta H = 96.18 \pm 1.82 \text{ kJ / mole}$$

In order to widen data which can be useful when studying the influense of substituents on thermodinamic characteristics of epoxy compounds heat of polymerization of epoxide containing substituted carbazole has been also established.To pursue this purpose 10 polymerizations of DBEPC in 1,2 - dichloroethane with different triphenylcarbenium salts was carried out. The values of heat of polymerization obtained are presented in Table 3.

No dependence of the values of heat of polymerization on conditions of the reactions was also observed for this monomer. The averaged value of polymerization heat of DBEPC is:

$$-\Delta H = 95.42 \pm 0.33 \text{ kJ / mole}$$

Table 3. Heat of Polymerization of DBEPC

Concentration of DBEPC, mole / l	Catalyst	Concentration of catalist, mole / l	Temperature ^{o}C	Conversion of DBEPC	Q, J	$-\Delta H$, kJ / mole
0.4	$Ph_3C^+BF_4^-$	0.02	30	0.692	26.531	95.85
0.4	$Ph_3C^+SbCl_6^-$	0.02	30	0.610	23.355	95.72
0.4	$Ph_3C^+SnCL_5^-$	0.02	30	0.852	32.503	95.37
0.1	$Ph_3C^+BF_4^-$	0.02	30	0.805	7.665	95.22
0.1	$Ph_3C^+SnCl_5^-$	0.02	30	0.880	8.349	94.86
0.1	$Ph_3C^+SbCl_6^-$	0.02	60	0.872	8.372	96.01
0.1	$Ph_3C^+SnCl_5^-$	0.02	60	0.821	7.822	95.27
0.1	$Ph_3C^+SbCl_6^-$	0.005	60	0.677	6.499	95.26
0.4	$Ph_3C^+BF_4^-$	0.005	60	0.541	20.664	95.49
0.4	$Ph_3C^+BF_4^-$	0.005	60	0.591	22.493	95.15

To verify the reliability of the values of polymerization heat of the carbazolyl-substituted epoxy monomers polymerization heat of 9-vinylcarbazole was established by the same procedure. The averaged value of $-\Delta H$ for this monomer was found to be 22.9 ± 0.85 kcal / mole, which satisfactorily agrees with the values established by Rodrigues and Leon (9). These authors investigated polymerization of 9-vinylcarbazole with triphenylmethyl hexafluoroarseniate and triphenylmetil hexafluorophospate and found $-\Delta H = 22.1 \pm 0.8$ kcal / mole at 20^{o} C.

Although the obtained values of polymerization heat for carbazole substituted epoxides are rather close, it is evident that $-\Delta H$ decreases in the row: EPC > ECOH > DBEPC.

According to Sawada (4) heat of reaction of polymerization which goes on with the opening of the cycle is determined mainly by the angular tension of the cycle, by conformational tension, by trans-annular tension which is connected with the overlaping of hydrogen atoms situated in the different sides of the cycle plane and by the steric effect of interaction of pendant substitues in polymer. In our case the last factor is apparently the main reason which determines the difference of the values of heat of polymerization of three substituted epoxy monomers studied in this work.

Acknowledgement

The authors are grateful to Professor S.Kutkevičius and dr. A.Stanišauskaitė for supplying 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane and 3,6-dibromo-9-(2,3- epoxypropyl)carbazole.

References

1. Vapšinskaitė, I.; Gaidelis, V. et. al. Zh. Nauchn. Prikl. Fotogr. Kinematogr., 1982, 27, 255.
2. Kavaliūnas, R.; Undzėnas, A.; Urbonavičienė, J. Zh. Nauchn. Prikl. Fotogr. Kinematogr., 1982, 27, 291.
3. Undzėnas, A.I.; Perelman, L.I.; Ruškys, D.D.; Popov, A.E. Lietuvos Fizikos Rinkinys, 1984, 24, 92.
4. Sawada, H. " Thermodinamics of Polymerization " Khimya, Moscow, 1979.
5. Zharov, Yu.M. " Thermodinamics of the Reactions of Polymerization and Polycondensation " - in " Thermodinamics of Chemical Processes. Oil-Chemical Synthesis, Proccessing of Oil, Coal and Natural Gas " Khimyia, Moscow, 1985.
6. Zherebtsov, I.P.; Lipina, Z.I. Manuscript deposited in ONIITEKhIM. 13 October 1980,

No 949 xp - D80.
7. Stanišauskaitė, A.; Leitaitė, A. deposited in LIMTI No 1403, 1985.
8. " Organic Solvents. Physical properties and Methods of Purification ", ed. by Weisberger, A., Interscience Publishers LTD, London, 1955
9. Calvet, E.; Prat, H. " Microcalorimetry Application in Physical Chemistry and Biology " Publishing House of the Foreign Literature, Moscow, 1963.
10. Rodrigues, M.; Leon, L.M. J. Polym. Sci.: Polym. Lett. Ed., 1983, 21, 881.

Accepted February 11, 1991 C