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POLYMERIZATION OF ACRYLONITRILE IN THE PRESENCE OF LITHIUM DIPROPYLBUTYLCARBINOLATE*

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THE initiating activity of alkali metal alkoxides is usually lower than that of the alkyls, as is evident in the polymerization of unsaturated hydrocarbons or acrylic esters. However, no data have been published in this connection such as would allow definite conclusions to be drawn in regard to characteristic features of the behaviour of alkoxides during acrylonitrile (AN) polymerization processes. Some data are given in papers [1–4] regarding AN–ROLi systems, but it would scarcely be possible, with the information so far available, to determine the special features of these initiators as opposed to those of butyllithium (BuLi).

It was found [1] that ROLi compounds may be used for the synthesis of high-molecular monodisperse polyacrylonitrile. In the present investigation our aim was to discover whether the use of ROLi initiators would obviate side reactions that are so characteristic feature of AN polymerization initiated by metal alkyls [5, 6]. Moreover, systems of the type studied are usually more suitable for investigation of the effect of dimethylformamide (DMFA) upon acrylonitrile polymerization processes; BuLi reacts with DMFA to form an alkoxide even at low temperatures, [7], and this greatly increases the difficulty of interpreting the results of investigations of AN polymerization processes in the presence of these initiators. At the same time the collection of data characterizing the effect of DMFA (varying from catalytic amounts to quite high DMFA contents) on the general course of AN polymerization processes is of major importance, seeing that the homogeneous low-temperature anionic polymerization of AN is possible only in DMFA medium.

This paper relates to an investigation of polymerization in the system AN–ROLi, as exemplified by lithium dipropylbutylcarbinolate (DPBL) in DMFA, in toluene, and in the presence of small amounts of DMFA. In toluene the initiating efficiency is as low as in a system in which BuLi participates (of the order of 1%). However, the reasons for this low initiating efficiency are not the same in both cases; a

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process initiated by BuLi takes place with a small amount of the metal alkyl expended in the formation of growing chains owing to side reactions (mainly oligomerization reactions [6]); DPBL is not consumed in side reactions, but the rate of initiation is very low. A major increase in the initiating efficiency is obtainable by carrying out the polymerization process in DMFA.

EXPERIMENTAL

The polymerization procedure and the purification of toluene and AN were described in [6]. DMFA after being kept for a long time over CaH_2 was vacuum-distilled, then dried once again over CaH_2, before being loaded into the reaction flask by means of a distributing manifold under vacuum.

DPBL was synthesized from dipropylketone and BuLi taken in equimolar amounts. The reaction was run under a countercurrent flow of argon, slowly adding the hexane solution of C_4H_9Li to the hexane solution of the ketone, and subsequently keeping the reaction mixture at 50° for 2 hr. After removal of the solvent the obtained alcoholate was vacuum-dried for 4–5 hr, with periodic heating to 80–100°. A working solution of the initiator was prepared by dissolving the alcoholate in freshly-distilled hexane: the solution was filtered through a Schott No. 4 filter and a Schlenk vessel.

The initiator which failed to enter into the reaction (during the AN polymerization) was identified as dipropylbutyl alcohol after the decomposition of the reaction mixture. The dipropylbutyl alcohol which after separation of the polymer and lithium chloride was isolated dy vacuum-distillation of the other products. The molecular weight of the polymers was betermined viscometrically, as in [8].

DISCUSSION OF RESULTS

The system AN–DPBL–toluene. There is a total lack of any data on the polymerization of AN in the presence of lithium alcoholates in toluene. It was therefore necessary to select an initiator which would ensure a reasonably efficient reaction in the low-temperature region. DPBL (which has not previously been used for this purpose) was found to be most suitable in this respect; the initiating activity of the other lithium alcoholates is noticeably lower than that of the compound in question (see Table 1).

Table 1. Polymerization in the systems AN–ROLi–toluene (Concentration, mole/l.; monomer—0·5; initiator 0·03 duration of the experiments, 2 hr)

Initiator	T, °C	Polymer, yield %	[η], dl/g
n-C_4H_9OLi	−50	0	—
	20	20	0·1
tert-C_4H_9OLi	−50	Traces	—
	20	17	0·1
DPBL*	−50	29	1·0

* The time of this experiment was 5 min.

The series of experiments were run with monomer and initiator concentrations of 0·3–2·5 and 0·001–0·2 mole/l. respectively, at —50°. The polymerization of AN in the system under review proceeds rapidly; under near-isothermal conditions the reaction takes place only if there is a monomer concentration of the order of 0·6 mole/l. (Fig. 1). We therefore limited ourselves to an attempt to determine the initiation efficiency F_n relative to different factors. The F_n values were calculated from the data on the yields and molecular weights of the polymers [6]. First we would draw attention to the marked rise in F_n with time accompanying the relatively slight rise in the molecular weight of the polymer along with the degree of conversion (see Table 2).

TABLE 2. EFFECT OF DIFFERENT FACTORS ON THE INITIATION EFFICIENCY IN THE POLYMERIZATION OF AN at —50° *

System	Concentration, mole/l.		Time of experiment, sec	Conversion, %	$\bar{M}\times 10^{-3}$	F_n, %
	initiator	monomer				
DPBL–toluene	0·01	0·65	3	3·5	104	0·1
	0·01	0·65	12	9·4	125	0·3
	0·01	0·65	300	27·5	176	0·5
	0·2	1·1	300	96	55–70	0·45
	0·03	1·1	300	55	180	0·55
	0·01	1·1	300	36	230	0·95
	0·001	1·1	300	25·2	300	4·4
	0·01	1·1	3	4·6	20*	1·2
C_4H_9Li–toluene	0·01	1·1	300	14	90	0·9
DPBL–toluene–DMFA	0·01	1·1	300	68	220	1·85
	0·01	1·1	300	84	190	2·6
	0·01	1·1	300	85·5	180	2·8
	0·01	0·65	5	15·3	107	0·5
	0·01	0·65	60	57	107	1·8
DPBL–DMFA	0·01†	1·0	300	100	120	4·0
	0·001†	1·1	300	100	330	16·0
	0·0001‡	1·1	300	20	70	98·5

* The mol. wt. of PAN prepared in the presence of BuLi at low monomer conversion is always slightly underestimated owing to the considerable size of the oligomer fraction which is present. This in turn leads to some overestimation of the value of F_n [6].

† Solvent for DPBL: A—hexane.

‡ B—DMFA.

Note. For the system DPBL–toluene–DMFA the ratio of DMFA : DPBL was 1, 3, 6, 3, 3 and 3 respectively.

All the above factors point to a low rate of initiation distinguishing DPBL from BuLi. In the case of initiation by BuLi under comparable conditions the magnitude of F_n remains practically constant, and the molecular weight of the polymer is practically a linear function of conversion (Table 2).

In view of the increasing initiation efficiency in the system AN–DPBL during the polymerization process, the relation of F_n to the reactants concentration was investigated with a standard time for the experiments. The relationship in question is a direct one in respect to monomer concentration (Fig. 2) but a reciprocal one in respect to initiator concentration (Table 2).

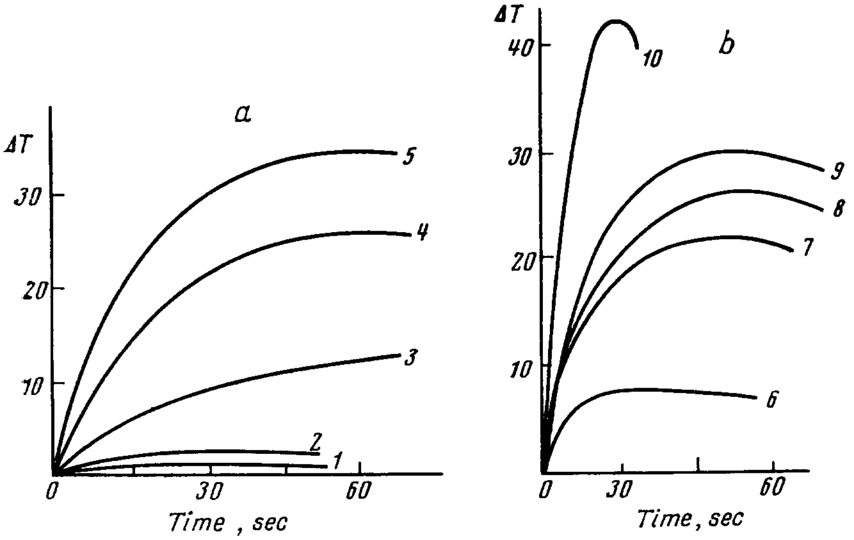


Fig. 1. Thermograms of AN polymerization in toluene (*1–9*) and in DMFA solution (*10*) with DPBL, the monomer concentrations being 0·3 (*1*), 0·6 (*2*); 1·1 (*3*, *6–10*); 1·6 (*4*) and 2·0 (*5*), initiator concentrations 0·03 (*a*) and 0·01 mole/l. (*b*), in the presence of DMFA (*7–9*), with DMFA/DPBL ratios of 1 (*7*); 3 (*8*); and 6 (*9*); $T_{\text{init}} = -50°$.

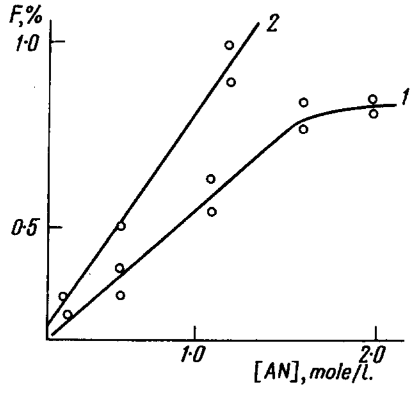
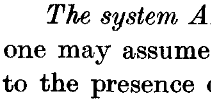


Fig. 2. Effect of monomer concentration of initiation efficiency in the system AN–toluene–DPBL, initiator concentrations 0·03 (*1*) and 0·01 mole/l. (*2*). Polymerization time 5 min.

Since the highest F_n value obtained by us for the system studied was not more than a few percentages (Table 2), it was desirable to ascertain whether the original initiator, like BuLi [5, 6], participates in the side reactions, or whether it remains unexpended. To do so we investigated the filtrates remaining after the polymer had been separated from the deactivated reaction mixture. The only product isolated in this way was dipropylbutylcarbinol (DPBC). No low-molecular products of the types normally appearing in the case of AN polymerization in the presence of BuLi were detected. The DPBC yield was 80% of theory, which agrees with the data obtained in the reference experiment where the initiator was broken down in the absence of monomer. With small initial DPBL concentrations ($\sim$0·0025 mole) it is not possible to obtain more complete separation of the DPBC with the method employed by us.

The following data were obtained by analysis of the DPBC, which has not previously been described in the literature.

Found, %: (reference experiment): C 76·6; H 13·8; O 9·6. Found, %: (polymerization experiments): C 76·5; H 13·8; 14·1; O 9·70, 9·40. $C_{11}H_{24}O$. Calculated, %: C 76·8; H 13·9; O 9·3. For DPBC obtained from the reference experiment n_D^{20} 1·4420; for the DPBC obtained from the polymerization experiment n_D^{20} 1·4425, d_4^{20} 0·8445, $MR_D=54·0$ (calculated 54·5). It was also found that the IR spectrum of the carbinol obtained in the reference experiment agreed well with that of the carbinol separated from the reaction mixture after the polymerization had been carried out.

It is noticeable that there is no simple relationship between the relative activities of the DPBL and C_4H_9Li initiators and the active centres formed as a result of their action. On comparing the data in Table 2 it would appear that the reactivity of the active centres on the growing chains was much higher in the case of initiation by DPBL. This follows from the much higher average molecular weights ($\bar{M}$) of the polymers formed in the system studied compared with the M values obtained in the same period of time under similar conditions with BuLi. This difference is apparently due to the much lower stability of a C–metal active bond in active centres formed in a system containing DPBL, these centres probably being in the form of ion pairs with a complex gegenion. We know that lithium alkoxides in solutions are in the form of very stable associates $(ROLi)_m$, where $m=6–9$, which are preserved even in polar media at elevated temperatures [9]. A structure of the type of $M_n—Li(ROLi)_{m-x}$, a fragment of which could be  $M_n—LiO\begin{smallmatrix} \diagup R \\ \diagdown Li \end{smallmatrix}$ therefore appears probable for the growing chains of the system studied. The conclusion that the reactivity of these growing chains is higher than that of $M_n—Li$ chains agrees with the actual findings reported in [10, 11] in regard to the activating effect of ROLi compounds on certain polymerization processes initiated by lithium alkyls.

The system AN–DPBL–DMFA–toluene. In the light of the available data [1] one may assume that unlike alkyl magnesium halides, which are very sensitive to the presence of small amounts of Lewis bases, including DMFA*, the effect

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* Catalytic amounts of DMFA greatly increase the overall efficiency of polymerization in the systems RMgX–AN [12–14].

of the latter on lithium alkoxides is appreciable only when considerable amounts of DMFA are used; as was noted above there are facts which point to the higher stability of $(ROLi)_m$ associates in polar solvents. The results of the respective experiments show, however, that even in the case of DMFA : DPBL=1, the initiation efficiency is approximately twice as high, which results in a higher reaction rate. On further increasing the DMFA concentration relatively smaller rises in F_n are observed (see Table 2).

Taking as an example DMFA : DPBL=3 it was found that in this case (as in the absence of DMFA) the F_n values increased with time (see Table 2). The initiation efficiency can be greatly improved by conducting the polymerization reaction in DMFA medium, using lower initiator concentrations for the experiments. This was particularly marked if instead of taking hexane solutions as the initiators, as in all the experiments described above (method A), we used a previously prepared solution in DMFA (method B). In the latter case the F_n values obtained for initiator concentrations of 0·0001 mole/l. are close to 100% (Table 2).

Strict intepretation of the above findings calls for detailed information regarding the molecular-weight distribution of the polymers formed under the conditions studied. At present we have only the preliminary results obtained for a small number of samples according to which poly-AN obtained in the presence of lithium alkoxides in DMFA medium is monodisperse (according to the results of turbidimetric analysis). In view of this one may reject the suggestion that chain transfer reactions are responsible for high values of F_n. The latter are probably due to the transition of DPBL into the monomeric form in the case of very low DPBL concentrations in DMFA. It should also be noted that data relating to a system in which DMFA participates are difficult to use for quantitative evaluation extending beyond the determination of F_n as there is a rapid and marked deviation of the temperature of the reaction mixture from the initial level owing to the high rate of the polymerization reaction.

CONCLUSIONS

(1) The investigation has yielded data characterizing the low-temperature polymerization of acrylonitrile (AN) in the presence of lithium dipropylbutylcarbinolate in toluene with the addition of catalytically small amounts of dimethylformamide (DMFA), and in DMFA.

(2) The initiation efficiency in toluene does not exceed 1%, owing to the low rate of initiation; the major part of the initiator remains unconsumed until the end of the polymerization process.

(3) The presence of catalytic amounts of DMFA improves the initiation efficiency quite markedly. By carrying out the polymerization in DMFA at a sufficiently low initiator concentration it is possible to achieve a practically complete utilization of DPBC for the initiation reaction.

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STUDY OF THE MOLECULAR STRUCTURE OF BUTADIENE-STYRENE THERMOELASTOPLASTICS*

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IN DETERMINING the molecular structure of copolymers it is necessary to elucidate specific molecular parameters which, together with molecular weight, molecular-weight distribution and the branching of the macromolecules, are the factors underlying the physical properties of copolymers. Factors of primary importance in this connection are the compositional inhomogeneity (compositional distribution) of copolymers and the alternation of chemically different units in the molecular chains. These parameters are of particular importance in the case of ionic copolymerization in which the structure of the chains may vary greatly according to the copolymerization conditions.

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