

Mechanism and Kinetics of Grafting of Macrodiisocyanate on to Carboxyl-Containing Acrylonitrile Copolymers

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Synopsis

The reaction of a carboxyl-containing acrylonitrile copolymer with a macrodiisocyanate based on polypropylene oxide ($M_n = 2000$) in dimethylformamide (DMFA) and dimethylsulfoxide (DMSO) solutions was studied. The mechanism and main kinetic regularities of the grafting reaction were investigated. The reaction proceeds through formation of a mixed anhydride with its subsequent decomposition leading to liberation of CO_2 and formation of graft copolymers. Carboxyl and nitrile groups of the copolymer take part in the reaction. A side reaction involving interaction of isocyanate groups of macrodiisocyanate with DMFA proceeds during synthesis of graft copolymers in DMFA solutions. The dependence of graft polymer yield on temperature, macrodiisocyanate concentration and on the catalyst/NCO ratio was determined. The activation energy of the grafting reaction is 22.9 kcal/mole. The specific viscosity of graft copolymers in DMFA solutions increases with the number of grafted chains.

INTRODUCTION

The synthesis of graft copolymers has been extensively used for modification of natural¹ and synthetic² fibers.

This method presents considerable interest for modification of polyacrylonitrile (PAN) fibers. It enables not only the removal of certain undesired properties, but also the endowment of PAN fibers with certain valuable properties (ion-exchange, fireproof, elastic, and antistatic properties). However, the absence of functional groups in PAN macromolecules that ensure formation of macroradicals, considerably hinders the use of traditional methods of graft copolymer synthesis predominantly based on radical graft copolymerization processes. In these conditions chemical addition of oligomers containing reactive terminal groups to PAN copolymers in homogeneous media is the most effective method of grafting. A considerable advantage of this method is that grafted chains directly participate in the formation of the superstructure of the modified fiber, thus improvising the physico-mechanical properties.

Chernukhina et al.³ recently obtained PAN copolymers grafted with polypropylene oxide by activating macrodiisocyanates with carboxyl-containing acrylonitrile copolymers. Fibers prepared from these grafts are highly resistant to multiple stresses.⁴

The present paper describes results obtained in the study of the kinetics and mechanism of the interaction of carboxyl-containing acrylonitrile copolymers with macrodiisocyanate based on polypropylene oxide.

EXPERIMENTAL

A ternary copolymer of acrylonitrile (AN) with methylacrylate (MA) containing 1.7% of itaconic acid was used as starting material. Macrodiisocyanate (MDIC) was prepared from polyoxypropylene glycol (molecular weight 2000) and 2,4-toluylenediisocyanate (TDI). The amount of free NCO groups in MDIC was 5.6%

Solvents (dimethylformamide and dimethylsulphoxide) were dried and distilled under vacuum. Triethylamine and triethylenediamine were used as catalysts.

Synthesis of Graft Copolymers

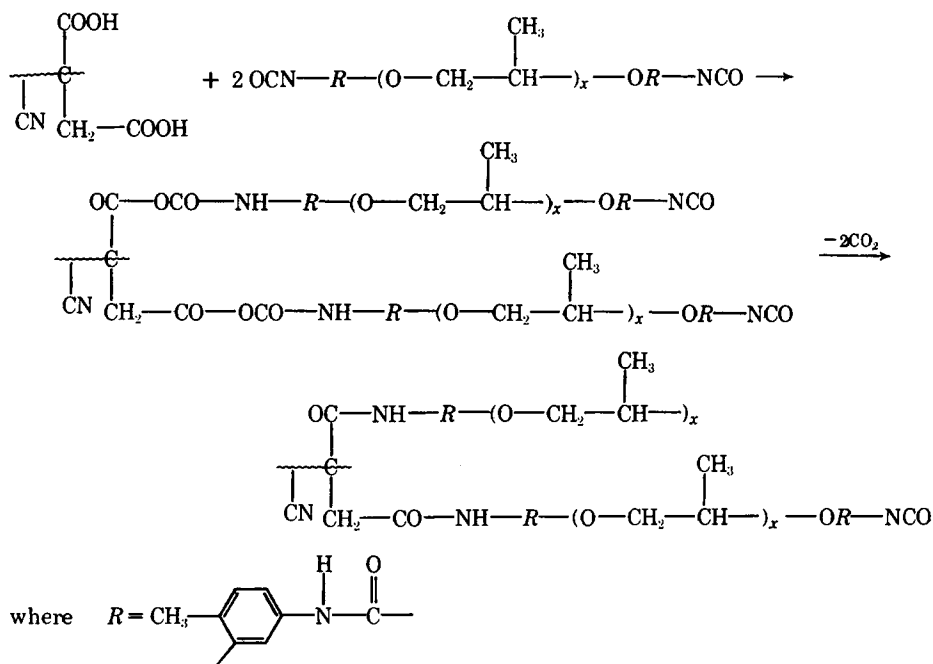
Grafting was carried out in a homogeneous medium in an inert atmosphere. To a 5% solution of copolymer in absolute DMFA the catalyst (triethylamine) was added (7% of the MDIC weight) and after mixing for 5–10 min the appropriate amounts of MDIC in absolute DMFA were introduced. The reaction mixture was precipitated in a large excess of methanol to remove unreacted MDIC, was repeatedly washed with methanol and dried at 25°C under vacuum.

Composition of the graft copolymers was characterized by the amount of nitrogen (Kjeldahl method) and carboxyl groups (by the nonaqueous titration method⁵).

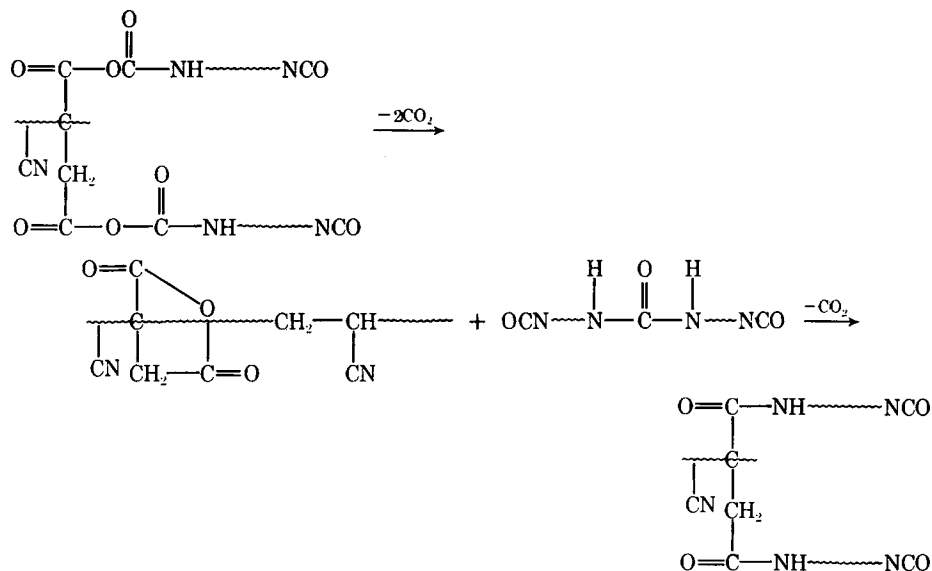
RESULTS AND DISCUSSION

It is known that low-molecular-weight isocyanate compounds react with carboxylic acids to form the corresponding substituted amides.⁶ The reaction is rather complex and its mechanism is still unclear. It proceeds through formation of various unstable derivatives. The nature and direction of subsequent decomposition depends to a considerable extent on the structure of the isocyanate and acid.⁷ Based on the mechanism of isocyanate reactions with carboxylic acids, the interaction of a macrodiisocyanate with carboxyl containing acrylonitrile copolymers to form graft copolymers may be represented as follows: (i) through

formation of a mixed anhydride with its subsequent decomposition:



(ii) through a mixed anhydride with subsequent evolution of CO_2 and formation of disubstituted urea and itaconic anhydride. Interaction between the latter two leads to the liberation of CO_2 and the formation of graft copolymers:



To establish the route of the reaction between MDIC and the copolymer and

TABLE I
Calculation of Conversion of Copolymer COOH Groups During Grafting in DMFA

N	Magnitude	Numerical value
1	Amount of COOH groups in initial copolymer (%)	1.150
2	Nitrogen content in initial copolymer (%)	24.3
3	CO ₂ equivalent corresponding to 100% conversion of COOH groups in 10 g of initial copolymer (g) (calculated)	0.1124
4	Amount of CO ₂ liberated during reaction of 10 g of copolymer with DMIC after 1 hr at 40°C (g) (experimental)	0.1492
5	Amount of COOH groups in graft copolymer obtained after 1 hr at 40°C (%)	0.527
6	CO ₂ equivalent corresponding to 10 g of grafted copolymer (g)	0.0514
7	Amount of COOH groups calculated according to the amount of liberated CO ₂ (% of theoretical) (0.1492 + 0.0514)/0.1124	177.8
8	Conversion of COOH groups calculated according to COOH content (%)	42.8
9	Nitrogen content in grafted copolymer (%)	17.54
10	Conversion calculated according to nitrogen content (%)	75

to determine the mechanism of the addition reaction to the copolymer, the amount of CO₂ liberated during the reaction was measured. CO₂ was blown out of the reaction mixture with dry argon, passed through a tube containing KY-2 resin to remove vapors of the catalyst, and absorbed by ascarite.

On addition of MDIC to the DMFA solution of the copolymer, CO₂ is rapidly liberated in quantities greatly exceeding the equivalent corresponding to 100% conversion of COOH groups in the copolymer; although, only 5% of the total amount of COOH groups participate in the reaction (Table I). The degree of conversion of carboxyl groups calculated from the amount of nitrogen in the graft copolymer is 75%. The fact that the conversion of COOH groups calculated according to the amount of nitrogen, carboxyl groups and liberated CO₂ do not coincide may be explained by side reactions. These reactions may be due to: (a) interaction of macrodiisocyanate with dimethylformamide; or (b) interaction of macrodiisocyanate with nitrile groups of the initial copolymer.

To determine whether macrodiisocyanate reacts with DMFA a comparative study was carried out of MDIC interaction with copolymer in DMSO and of MDIC reaction with DMFA in the absence of copolymer.

On addition of MDIC to DMFA in the absence of copolymer, CO₂ is liberated at relatively low temperatures (40°C) even in the absence of a catalyst (Table II). Introduction of a catalyst and the addition of a copolymer solution leads to additional evolution of CO₂. Therefore, it can be concluded that during synthesis of graft copolymers in DMFA the appreciable amount of CO₂ liberated is due not only to the interaction of NCO groups with carboxyl groups of the copolymer, but also to a reaction of isocyanate groups of MDIC with DMFA. The mechanism of this reaction may be described by the scheme⁸:

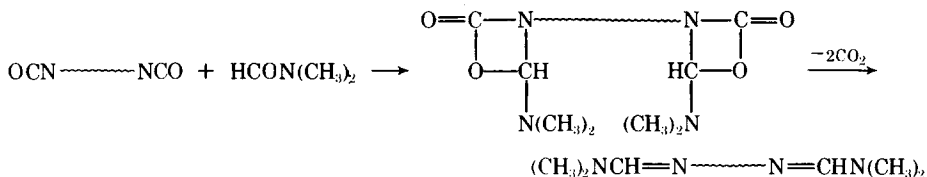


TABLE II
Amount of CO₂ Liberated During Interaction of MDIC with DMFA in the Presence of Catalyst and Copolymer

Reaction time (hr)	Amount of CO ₂ liberated (%)		
	DMFA + MDIC	DMFA + MDIC + catalyst	DMFA + MDIC + catalyst + copolymer
1	0.0350
2	0.0066
3	...	0.0067	...
4	...	0.0156	...
5	...	0.0038	...
6	...	0.0021	...
7	0.0072

This reaction proceeds only in DMFA.

Synthesis of graft copolymers in DMSO is also accompanied by rapid liberation of CO₂; however, this is due to the interaction of isocyanate groups only with the carboxyl groups of the copolymer. This is indicated by the good correlation between the amount of reacted COOH groups and those remaining in the graft copolymer (Table III).

Intensive evolution of CO₂ during interaction of MDIC with the AN copolymer at relatively low temperatures, combined with the fact that interaction of disubstituted urea with anhydrides to form amides occurs only at high temperatures⁹, suggests that interaction of MDIC with carboxyl groups of the copolymer (during synthesis of graft copolymers) follows the first and not the second route.

Conversions calculated according to the amount of carboxyl groups and nitrogen in the grafted copolymers synthesized in DMFA and in DMSO differ considerably (Tables II and III). Thus, not only do carboxyl groups take part in the grafting reaction, but isocyanate groups of MDIC also partially interact with nitrile groups of the copolymer is given reaction conditions.

TABLE III
Calculation of Conversion of Copolymer COOH Groups During Grafting in DMSO

N	Magnitude	Numerical value
1	Amount of COOH groups in initial copolymer (%)	1.150
2	Nitrogen content in initial copolymer (%)	24.3
3	CO ₂ equivalent corresponding to 100% conversion of COOH groups in 10 g of initial copolymer (g) (calculated)	0.1124
4	Amount of CO ₂ liberated during reaction of 10 g of copolymer with MDIC after 1 hr at 40°C (g) (experimental)	0.0614
5	Amount of COOH groups in grafted copolymer after 1 hr, 40°C (%)	0.546
6	CO ₂ equivalent corresponding to 10 g of grafted copolymer (g)	0.0534
7	Fraction of reacted COOH groups $0.0614/0.1124 =$	0.55
8	Amount of COOH groups calculated according to the amount of liberated CO ₂ (% of theoretical) $(0.0614 + 0.0534)/0.1124$	102
9	Conversion of COOH groups calculated according to COOH content (%)	42.8
10	Nitrogen content in grafted copolymer (%)	15.73
11	Conversion calculated according to nitrogen content (%)	100

This assumption is supported by formation of a graft copolymer during interaction of MDIC with acrylonitrile homopolymer in DMSO in similar conditions (Table IV). IR spectra of the obtained graft copolymer exhibit bands characteristic of urethane groups formed as a result of blocking the terminal isocyanate groups of grafted chains with methanol (Fig. 1).

Interaction of macrodiisocyanate with acrylonitrile copolymers in DMFA proceeds in a more complex manner: the formed oligomer product containing end amide groups may react in DMFA with nitrile groups of the copolymer macromolecule to yield a graft copolymer. This is confirmed by the small amount of CO_2 liberated in the reaction of MDIC with DMFA (Table II) and on subsequent addition of copolymer solution in DMFA to the reaction mixture. This procedure renders graft copolymers containing eight side chains per 10^3 mer units.

Interaction of MDIC with AN copolymer in DMFA may follow various routes. The variation of nitrogen content in the graft copolymers was used as the main criterion in the study of the effect of temperature, reaction time, NCO:COOH ratio, solvent and catalyst on the amount of grafted chains.

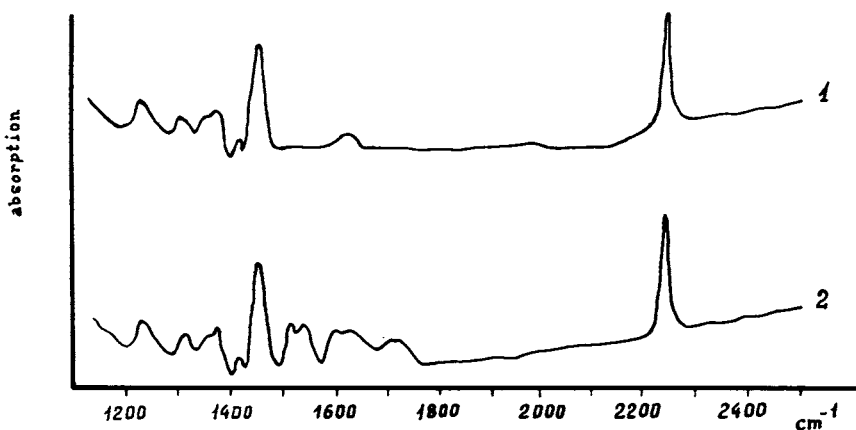


Fig. 1. IR spectra of PAN (1) and graft PAN copolymer (2).

TABLE IV
Effect of Duration of PAN Interaction with MDIC on Nitrogen Content^a

Reaction period (hr)	Nitrogen content in reaction products (%)	Conversion of CN groups (%)	Number of grafted chains per 10^3 mer units
0	26.1
1 ^b	20.4	0.7	7
1	21.5	0.6	6

^a PAN = 4.25×10^{-1} mole/liter; MDIC = 7.38×10^{-3} mole/liter; triethylenediamine = 1.08×10^2 mole/liter; reaction temperature, -40°C ; nitrogen medium.

^b Reaction was carried out in DMFA.

Effect of Temperature

The reaction temperature significantly affects the grafting process. The degree of carboxyl group conversion sharply increases with temperature (Fig. 2). However, the probability of side reactions with DMFA also apparently increases, leading to a reduction in the amount of grafted chains. This is indicated by the smaller amount of grafted chains in copolymers obtained at 50°C than at 40°C regardless of the reaction period.

Effect of the NCO:COOH Ratio

The dependence of the amount of grafted chains and copolymer yield on the NCO:COOH ratio is shown (Table V). At higher NCO:COOH ratios in the reaction mixture, the amount of grafted chains and the yield of graft copolymer increase. For instance, grafts containing eight grafted chains of polypropylene oxide ($M_p = 2000$) per copolymer molecule are obtained at a ratio of NCO:COOH = 2.

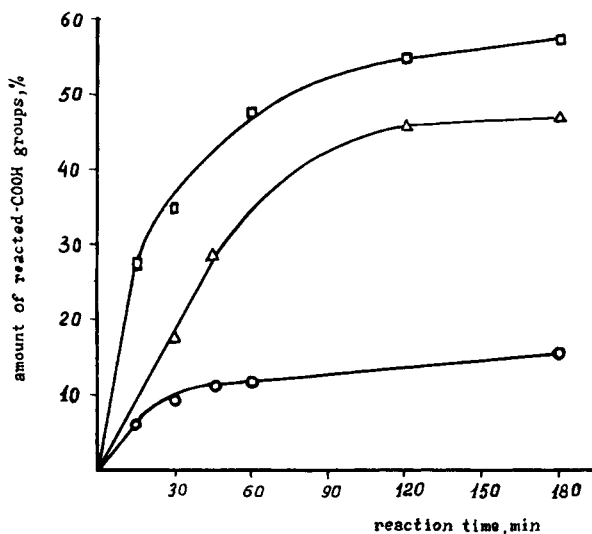


Fig 2. Effect of grafting temperature on the amount of reacted COOH groups. ○, 30°C, ●, 40°C, △, 50°C. AN copolymer = 5%; triethylamine = 7% of MDIC weight; NCO:COOH ratio = 2.5.

TABLE V
Effect of NCO:COOH Ratio on the Amount of Grafted MDIC^a

NCO:COOH	Nitrogen content in grafted copolymer (%)	Amount of reacted COOH groups calculated according to nitrogen content (%)	Number of grafted chains per 10 ³ mer units	Amount of grafted polymer (%)
0.63	23.11	10.0	1.4	6.3
1.25	22.50	15.2	2	9
2.50	18.76	57.1	8	36

^a Reaction period = 3 hr; temperature = 40°C; concentration of initial copolymer in solution = 5%; triethylamine concentration 7% of MDIC weight.

TABLE VI
Effect of Solvent on the Amount of Grafted Chains^a

Solvent	<i>E</i>	Content in grafted copolymer		Number of grafted chains per 10 ³ mer units calculated from	
		COOH (%)	N (%)	COOH content	nitrogen content
DMFA	37	0.53	17.34	8	11
DMSO	49	0.55	15.73	8	14

^a COOH content in the initial copolymer = 1.15%; MDIC = 64×10^{-2} mole/liter; triethylenediamine = 2.4×10^{-2} mole/liter; AN copolymer = 5%; reaction period = 1 hr.

Effect of Solvent and Catalyst

Interaction of isocyanate groups with terminal carboxyls of oligomers in the presence of a catalyst proceed more rapidly in solvents with a low rather than high dielectric constant.¹⁰ However, interaction of carboxyl-containing AN copolymers with MDIC proceeds more quickly in such polar solvents as DMFA ($E = 37$) and DMSO ($E = 49$). Nearly 50% of the carboxyl groups enter into a reaction during the first hour (Tables I and II). This may be explained by the increase of nucleophilicity of initial copolymer carboxyls due to solvation by solvent molecules that leads to an increase in the reaction rate. Solvents with high polarity similarly affect nitrile groups, thus creating favorable conditions for interaction of nitrile groups with isocyanate groups of MDIC. This is supported by the considerably higher amount of grafted chains as calculated according to nitrogen content in graft copolymer than according to the carboxyl content. The difference increases with the polarity of the solvent (Table VI). The assumption that nitrile groups react with MDIC is also confirmed by data presented in Table IV. Six chains of polypropylene oxide are grafted to AN homopolymer in one hour.

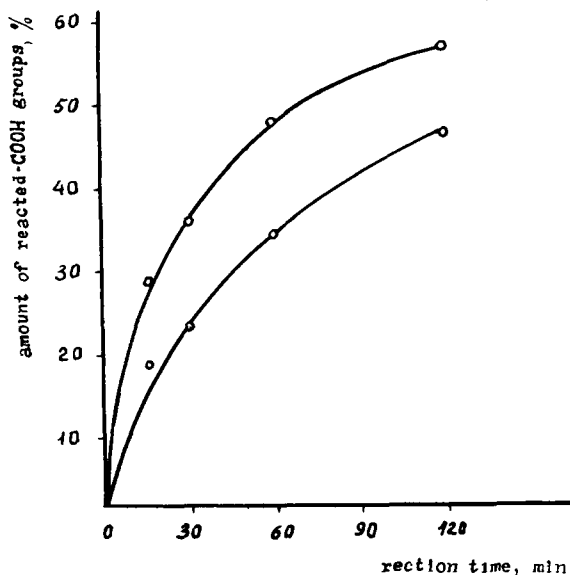


Fig. 3. Effect of reaction time on the amount of reacted COOH groups. ●, without catalyst; ○, with catalyst. AN copolymer = 5%; triethylamine = 7% of MDIC weight; reaction temperature 40°C; NCO:COOH ratio = 2.5.

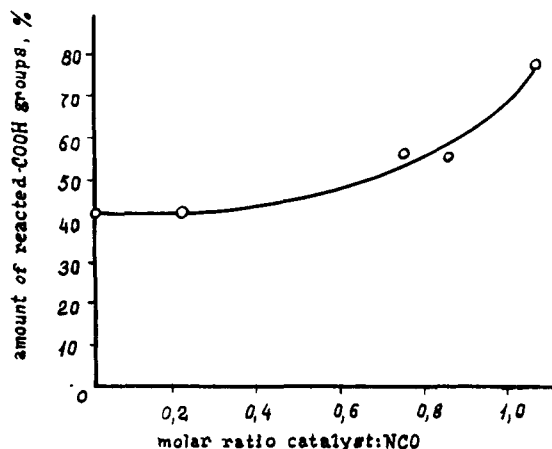


Fig. 4. Effect of triethylenediamine:NCO ratio on the amount of reacted COOH groups. AN copolymer = 5%; reaction temperature = 40°C; reaction period = 3 hr; NCO:COOH ratio = 2.5.

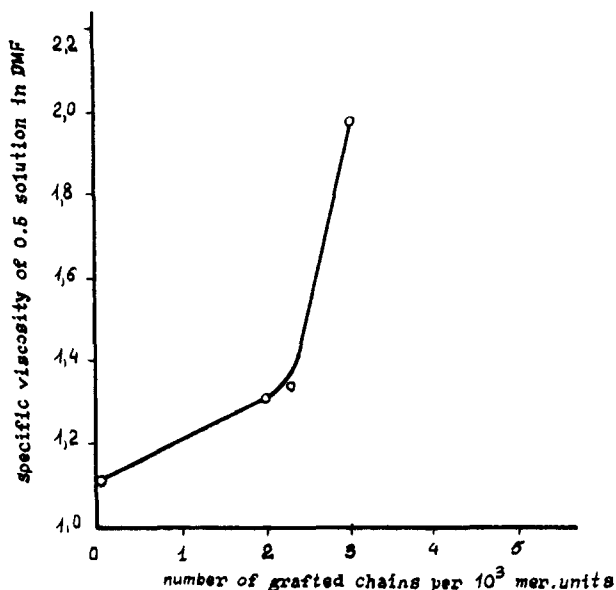
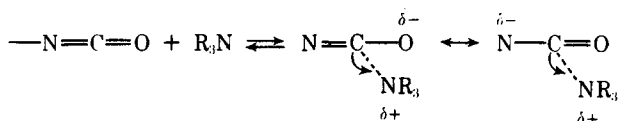


Fig. 5. Dependence of specific viscosity of 0.5% DMFA solution of graft copolymer on the number of grafted chains per 10³ mer links. AN copolymer = 5%; triethylamine = 7% of MDIC weight; reaction temperature = 30°C; NCO:COOH ratio = 2.5.

MDIC interaction with AN copolymer in DMFA proceeds at relatively high rates even in the absence of a catalyst. Although the rate of MDIC addition to the copolymer increases, the effect of triethylenediamine is less than could have been expected for such a strong catalyst¹¹ (Fig. 3).

The rate of grafting reaction increases with the catalyst:NCO ratio (Fig. 4). The catalyst presumably interacts with isocyanate groups forming an intermediate complex:



This significantly reduces electron density on the carboxyl carbon atom, thereby accelerating the addition of isocyanate groups to the copolymer carboxyl groups.

Grafting of side chains with a relatively low molecular mass ($M_p = 2000$) leads to an increase of specific viscosity of grafted copolymers in DMFA. The greater the number of grafted chains, the greater is the specific viscosity (Fig. 5).

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