Synthesis, properties and applications of Halogen containing polyimides

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Abstract

The new approach for synthesis of novel condensation monomers and polyimides on the basis of them was developed. The correlation between synthesis regularities, structure and properties of monomers and polyimides was studied. The areas of industrial application of synthesized polymer were determined.

Introduction

In the laboratory of polymer synthesis of Chemical Sciences Institute of Kazak Academy of Sciences the synthesis technology of the benzene photoadduct and its halogen (chlor-, fluor-), aryl-, alkyl- substitutes and maleic anhydride under solar energy (or mercury-quartz lamps) effect are developed. The photoadducts are dianhydrides of the tetracarbonic acids actively reacting with diamines. On the base of photoadducts the polyimides have been obtained with a complex of valuable properties, polyimide lacquers and materials: polyimide films, enamel wires, glass plactics etc.

The principal synthetic method for dianhydrides of alicyclic tetracarboxylic acids is the cyclo- addition reaction with polyenes, in which -bonds are formed due to the opening of -bonds in the addends. Such processes take place particularly during the diene condensation reaction, i.e. dienic synthesis or the Diels-Alder reaction. The use of maleic anhydride (MA) as a dienophile in the Diels-Alder reaction allows a wide range of possibilities to be condidered for the synthesis of anhydrides of various alicyclic polycarboxylic acids. The application of aromatic and heterocyclic compounds in the capacity of dienes, which permits the synthesis of dianhydrides of alicyclic tetracarboxylic acids, used subsequently to obtain heat-resistant polyheterocycles, is of special interest in the contex of this review.

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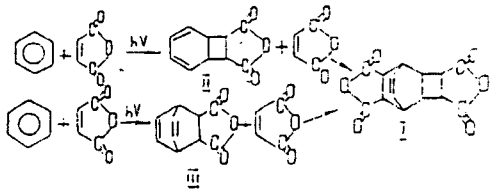
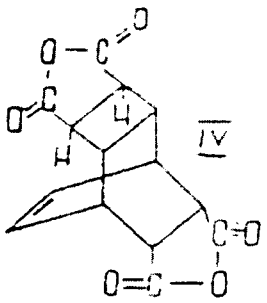
Discussion

In 1959 a review by Angus and Bryce-Smith [1] was the first report of the production of stable adducts of benzene with maleic anhydride of composition 1:2 by photochemical method. It has been noted that the reaction of photoaddition of maleic anhydride to benzene can be achieved in two ways.



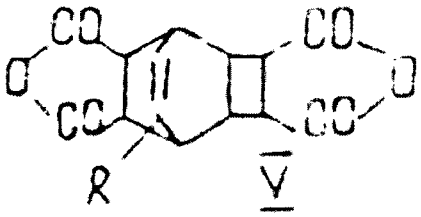
The intermediat adduct III is less inclined to undergo addition of the second molecule of maleic anhydride than the initial reaction. Strongly shielded double bond is detected by NMR spectroscopy and chemically using the slow addition reaction of bromic water. It has been shown that adduct I has the spatial structure IV. This view is shared by Bryce-Smith et al [2].



IV

This reaction can be sensitized by a number of compounds, having a ring with a resonance structure. Among them there are aromatic aldehydes and ketones (benzaldehyde, acetophone (APh), and also diarylketones, benzophenone and number of its substituted compounds). Benzophenone and acetophenone rank among the most effective reaction sensitizers. In the presence of benzophenone the reaction proceeds upon solar irradiation with a high yield of photoadduct, 93 % after 78 hr irradiation.

A number of researchers have shown that maleic anhydride can paticipate in the reaction of photoaddition not only to benzene, but also to other aromatic hydrocarbons. thus stable photoadducts (2:1) of maleic anhydride have been obtained with toluene, tetrabutyl-benzene, chlorobenzene, o-, p-xylols, diphenyl, quinol. The composition and stereochemistry of the photoadducts have been examined by chemical and physical studies. According to these data the photoadducts are generally related to a series of 7-p-tricyclo (4,2,2,0)decene-7 with the P-substituent located at the double bond.



V

Quantitative determination has been carried out of quantum yields of the photosensitized addition of maleic anhydride to benzene, toluene, cumene, chlorobenzene and diphenyloxide in the solution of the inert solvent-dioxan. Acetophenone has been used as a sensitizer. Maximum values of quantum yield in optimum conditions (i.e. at MA:APh:A = 1:1:10) are given below.

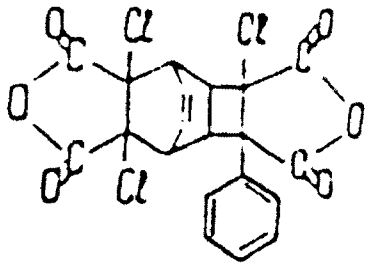
Aromatic hydrocarbon	quantum yield, Ph
Benzene	0.120
Toluene	0.080
Cumene	0.070
Diphenyloxide	0.015
Fluorobenzene	0.040
Chlorobenzene	0.030

The regularity observed for the adduct formation makes it possible to optimize the reaction for the synthesis of new dianhydrides of alicyclic tetracarboxylic acids (Table 1).

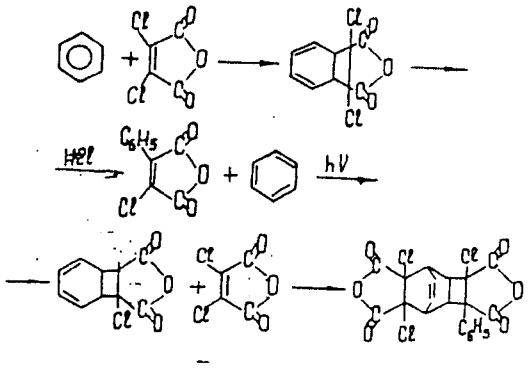
Table 1. Characteristics and Synthesis Conditions of Maleic Anhydride Adducts with Different Aromatic Hydrocarbons at 50-60℃ [3-4]

Aromatic hydrocarbons (diene)	Reaction condition, hours	C mol/L sensitizer	Yield %	Melting T ℃
Benzene	10	0.10	95.0	354
Toluene	15	0.10	80.0	265-270
Propylbenzene	40	0.15	85.0	250-255
Hexylbenzene	25	0.20	70.0	250-255
Diphenyl	30	0.30	50.0	280-285
Diphenyloxide	25	0.30	65.0	285-290
Fluorobenzene	15	0.50	68.0	310-315
Chlorobenzene	20	0.50	56.0	290-295
p-Fluorotoluene	25	0.45	35.0	290-295
o-Chlorotoluene	30	0.35	25.0	256-258

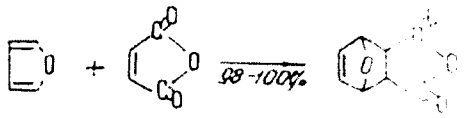
The use of dichloromaleic anhydride (DChMA) as a dienophile results, contrary to expectations in the formation of dianhydride of tricyclode-centetracarboxylic acid, containing three, not four, chloro atoms.



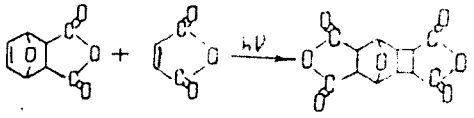
It has been established [5] that in this case the reaction proceeds in the following way



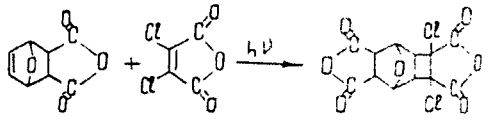
ABDCh with m.p. 288-290 ℃ is obtained in 50% yield upon irradiation of a DChMA solution in benzene for 30 h at 25-30 ℃ in the presence of benzophenone and aromatic hydrocarbons, heterocyclic compounds, in particular, furan are also obtained. It is well known that by the diene condensation of furan with MA, there is forms in quantitative yield, the anhydride of 7-oxo-bicyclo(2,2,1)-hept-5-ene-2,3,-dicarboxylic acid (MAF) [3,6]



The compound (MAF) obtained upon UV irradiation in the presence of sensitizers adds a second molecule of maleic anhydride with the formation of dianhydride of 9-oxytricyclo (4,2,1,0)-nonane-3,4,7,8-tetracarboxylic acid (AF)



The possibility of photochemical addition dichloromaleic anhydride to MAF with the formation of 3,4-dichloro-9-oxytricyclo-(4,2,1,0) - nonane 3,4,7,8-tetracarboxylic acid (AFDCh) has been also showed.



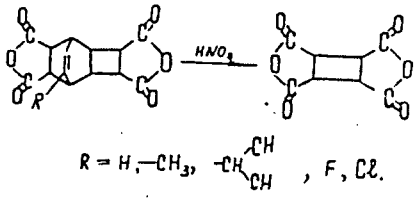
MAF has proved to be a very active compound. It has been shown that in the presence of the sensitizers MAF dimerized with the formation of dianhydride of 9,14-dioxypentacyclo-(8,2,1,1,7,0,0) -tetradecan-5,5,12,13-tetracarboxylic acid occurs. Optimum conditions for the synthesis of anhydrides based on furan and some of their properties are represented in Table 2.

Table 2. Conditions for Anhydrides Synthesis on the Base of Furan

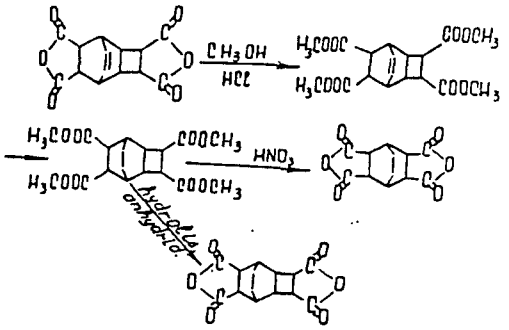
Dianhydride	Sensitizer	Irradiation duration, h	Yield, %	Tm, ℃
MAF	-	without 2	99.0	125
AF	Acetophenone	30	45.0	410
	Benzophenone	30	60.0	
	Benzophenone	Sunshine, 70	40.0	
DOBS	Acetophenone	40	15.0	370
	Benzophenone	40	30.0	
	Benzophenone	Sunshine, 70	30.0	
AFDCh	Acetophenone	20	60.0	310
	Benzophenone	30	27.0	312

The chemical structure of dianhydrides of tricyclodecentetracarboxylic acids can be modified allowing the synthesis of new dianhydrides. For example, the oxidation by nitric acid of the dianhydride leads to the formation of cyclobutantetracarboxylic

acid, irrespective of the composition of initial dianhydride [7].



Reactions with the endoethylenic group can serve as another example of AB modification. In this case it is convenient to first increase solubility of the tetramethylic ether and then subject it to chemical transformation: hydrogenation, oxidation, hydrolysis [8].



Synthesis of the alicyclic polyimides in the polar aprotic solvents of amide type by means of an one-stage method has been offered as a new synthetic method. This method is based on an activation of polycondensation by tertiary amines, carboxylic and pyridinecarboxylic acids, ethers and cyclic ethers. Thermal, physico-mechanical and electric properties of synthesized polymers have been studied. An effect of plasticizer on the main characteristics of the polyimides has been determined.

Conclusions

The investigations to use the solar energy for chemical technologies and new monomer synthesis were carried out. Dianhydride of alicyclic tetracarboxylic acids have been used for the synthesis of new polyheterocycles. As a result, new polyimide lacquers for production of a wide number of technical articles, such as polyimide films, fibres, enamel-wires, press-materials have been synthesized. An application field of the halogencontaining alicyclic polyimides in membrane technology, print plate and optic electronics manufactures has been outlined.

References

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