Introduction Aromatic polyamides and polyimides are widely used in modern industry due to its excellent mechanical properties, high thermal and chemical stability. However, many of these polymers are difficult objects for processing because of their infusibility and insolubility in organic solvents. In this regard, great interest of polymer chemistry to new, fully aromatic structures that would preserve their inherent high level of physical-mechanical properties and at the same time would be fusible and easily soluble in organic solvents is understandable. One of monomers, which may be of interest from this point of view, is 4,4’-diaminothreephenylmethane. Although the details of this monomer synthesis were published in 1928 [1], there are very few works on its use in the polycondensation reactions [2,3]. Meanwhile, it is shown that the aromatic polyimides and polyamides on the basis of aromatic diamines of similar structure, such as N,N’-diaminothreephenylmethane [4,5] and N,N’-diaminotetraphenylmethane [5] can be easily soluble in organic solvents, and have a range of interesting properties. However, it should be noted that the synthesis of these monomers is quite complex. Unlike the above monomers, 4,4’-diaminothreephenylmethane can easily be obtained in one stage of available connections with high output. The present research is devoted to the synthesis of aromatic polyimides and polyamides-based 4,4’-diaminothreephenylmethane and study their main properties as solubility and mechanical characteristics. The experimental part All reagents were obtained from ALDRICH Company. Aniline was surpassed in vacuum (87 oC, 1 mm Hg.) before its use. Benzaldehyde was used without treatment. Iso- and tetraphthalic chloroanhydrides was distilled at 170 oC (57 mm Hg) and at 165 oC (50 mm Hg), respectively. Pyromellitic of dianhydride was double-sublimated at 245 oC (10-4 mm Hg.). Dichlorohydrin of diphenylcarbazone acid of firm ALDRICH (the degree of purity 98%) was used without treatment. N-methylpyrrolidone was ferried over barium oxide BaO at 98 oC (20 mm Hg ) and was kept over CaCl2. Synthesis 4,4’-diaminothreephenylmethane 4,4’-diaminothreephenylmethane was synthesized by the reaction of aniline with benzaldehyde at 140 oC in nitrogen atmosphere. The details of its synthesis is described in works [1,2]. Received 4,4’-diaminothreephenylmethane was purified by recrystallization from benzene followed by sublimation at 110 oC (10-4 mm Hg). Elemental analysis results agree well with the structure of the monomer. 83,15; N - 6,47; N - 10,17 was found (%). C - 83,17; H - 6,61; N - 10.21 was calculated (%). Synthesis of polyamide-based on 4,4’-diaminothreephenylmethane 4,4’-diaminothreephenylmethane was dissolved in a dry N methyl-pyrrolidone and cooled to 0 oC. Stoichiometric amount of dichlorohydrin Iso - or tetraphthalic acid were added to the solution in the mixing and were raised to the room temperature (reaction time 4-5 hours, the concentration of polymer in the solution 15% weight). Received polyamides were undercooled from N - methylpyrrolidone. The solutions of treated polymers in N - methylpyrrolidone (20% weight) were put on glass plates and were dried at 150 0C in vacuum (50 mm Hg) for 10 hours. Synthesis of polyimides based on

4,4’-diaminothreephenylmethane Polyimide films were synthesized in two stages by chemical or thermal imidization of prepolymers - polyamid acids (PAA) [4, 7, 8]. The degree of imidization we controlled with IR spectroscopy [7]. The output of polyimides is close to quantitative (about 100%). Measurements The Intrinsic viscosity (ɳin, dL/g) we were determining in the solution of dimethylformamide (0.5 g per 100 ml of dimethylformamide) at 25 0C. IR - spectra were taken on the spectrometer NICOLET 510 FT - IR. X-ray spectra of polymers were received on the diffractometer Siemen's D - 500 c CuK. Data of thermogravimetric analysis were obtained using the device Du Pont 2950 (in nitrogen atmosphere, the heating rate is 5 C/min). Glass transition temperature polymers (TD) was determined from the results of thermomechanical analysis on the device Du Pont 2950 in nitrogen atmosphere at heating rate 50 0C /min using technology oriented films [9]. Mechanical properties of polymer films (samples 30x40 mm) was determined on the device INSTRON 111 at speeds stretching 50 mm/min. Theoretical calculations Structural parameters and the rotation barriers of phenyl rings around the Central carbon atom of 4,4’-diaminothreephenylmethane were calculated using supercomputer SKOU. After full minimization according to molecular method MMX-89 [10] the structure were optimized by semi empirical method of molecular orbitals AM1 [11]. Results and discussion Structural parameters and energy barriers of rotation on the Central carbon atom were calculated for 4,4’-diaminothreephenylmethane to evaluate the possibility of rotation of fragments of a polymer chain around the bridged group of 4,4’-diaminothreephenylmethane. The data obtained show that SP3-hybridization of the Central carbon atom leads to the pyramidal structure of the molecule 4,4’-diaminothreephenylmethane. The estimated value of the angle C2 C1 C3 in the molecule is 112,070, which is very close to the calculated 4,4’-diaminothreephenylmethane [12]. It is found that the energy barrier of rotation around the Central atom in 4,4’-diaminothreephenylmethane is of 5.89 kcal/mol, which is rather close to those of 4,4’-diaminodiphenylmethane or 4,4’-diaminodiphenylamine [13]. The results obtained agree well with the experimental data on the flexibility of polyimide circuit-based 4,4’-diaminothreephenylmethane [5]. Equilibrium flexibility (σ) of these polymeric structures amounted to no more than 1,10 indicating almost free internal rotation (from the point of view of thermodynamics) polymer chains. Some of these polyimides have a good solubility in organic solvents. Table 1 presents data of solubility aromatic polyimides and polyamides-based 4,4’-diaminothreephenylmethane in various organic solvents at room temperature. It should be noted that the polymers of such structures on the basis of known diamines type 4,4’-diaminothreephenylmethane or 4,4’-diaminothreephenylmethane are insoluble in organic solvents, and solubility of polyimides (polyamides) on the basis of 4,4’-diaminothreephenylmethane can be explained by the effect of volume phenyl rings in the monomer molecule. This monomer, apparently, can be considered as a representative of the so-called “cardoided diamines” [14], which is known for obtaining soluble polyamides and polyimides. Table 1 - Solubility* polyamides and polyimides based on4,4’-diaminothreephenylmethane Polymer solvent Dime thyl formamide N - methyl pyrrolidone Pyridin Tetrahy drofuran Acetone 3h1d7d 3h1d7d 3h1d 7d 3h 1d7d 3h 1d7d 1 ++++ +++ ++++ - p.s + - -- 2 ++++ +++ ++++ - p.s + - - 3 ++++ +++ ++++ - -p.s - p.s 4 ++++ +++ ++++ - - - - p.s 1 - , 2 - , 3 - , 4 - *- solubility were checked after 3 hours., 1 day and 7 days at room temperature; (+) - completely soluble, (-) - insoluble, (p.s) - partially soluble. Polyamides-based on 4,4’-diaminothreephenylmethane have better solubility than polyimides on the basis of the same monomer. The latter gives the possibility to prepare solutions polyamides with concentration up to 30-35% wt. in such amide solvents as the N- methylpyrrolidone or dimethylformamide. Solubility of received polyamides in pyridine and tetrahydrofuran is much lower. Polyamides are insoluble in acetone, and in the presence of even small amounts of solvent polyamide films become extremely fragile. The observed fact, apparently, is the result of weakening inside of the sample molecules acetone intermolecular by hydrogen bonds between the amide groups in polymers, responsible for the mechanical properties of the ground state. In the case of polyimides synthesized by chemical imidization the samples are easily soluble in amide solvents (maximum concentration 15-20 weight. %), in pyridine and swell in the dichloroethane. It should be noted that previously it was reported about insolubility of polytriphenylaminepyromellitics [5] and, it seems that polyimide synthesized by us which based on 4,4’-diaminothreephenylmethane is one of the few which is soluble in organic solvents. Solubility of synthesized polyimides by thermal imidization is much worse. Samples of polyimide films which were prepared at a temperature of 270 0C for 30 min (further increase in the temperature does not increase the degree of imization, which is close to 100%) are only partially soluble in dimethylformamide or N-methylpyrrolidone and inert in other solvents. The number of insoluble fraction increases with increasing temperature or increase time of thermal processing. A similar effect was observed after annealing higher than the temperature of 270 0C of completely soluble polyimides, synthesized by chemical imidization at room temperature. Thus, we can conclude that the polyimides based on 4,4’-diaminothreephenylmethane are heat-stitching at temperatures above 270 0C, just as previously we observed for other polyimides [8,12]. Table 2 shows the thermal properties of the synthesized polymers on the basis of 4,4’-diaminothreephenylmethane. Table 2 - Thermal properties of polyamides and polyimides based on 4,4’ - diaminothreephenylmethane №/№ Polymer glass transition temperature, Tg, °C weight loss*, 5% weight loss*, 10% I 1 177 238 470 II 2 231 449 474 III 3 288 516 538 IV 4 356 538 564 1 - , 2 - , 3 - , 4 - *-weight loss polymers were identified in nitrogen atmosphere at heating rates of 5 0C/min The results of thermomechanical analysis show that all polymers show distinct differences in glass-transition temperature. In particular, the values of glass transition temperature increase in the range of dichlorohydrin isophthalic acid - 4,4’-diaminothreephenylmethane (I), dichlorohydrin terephthalic acid - 4,4’-

diaminothreephenylmethane (II), 4,4’-dichlorodiphenyldichloroethane acid - 4,4’-diaminothreephenylmethane (III), pyromellitic of dianhydride - 4,4’-diaminothreephenylmethane (IV). Glass transition temperature of the synthesized polyimides was determined on prepared by chemical imidizaion samples. The values of glass transition temperature Tg are very close to values of glass transition temperature Tg of polyimides, obtained on the basis of known diamines type 4,4’ diaminothreephenylmethane [12, 15] previously published in the literature. According to the DTA and TGA the thermal destruction of polimers which synthesized on the basis of 4,4’-diaminodiphenylmethane in nitrogen atmosphere is beginning at temperatures above 400 0C (table. 2). The greatest resistance of all investigated polymers is observing for polyimide based on benzene tetracarboxylic dianhydride and 4,4’-diaminothreephenylmethane (IV). The values of temperatures given in table. 2 in which there is a 5 and 10 % weight loss of polymers in an inert atmosphere, only slightly lower than industrial polyimide film KAPTON HN ( For KAPTON these values are 545 0C and 573 0C, respectively) [16]. Results of mechanical tests of polymer films with thickness of 25 microns are shown in table 3. Studies have shown that the obtained polymers have a fairly high mechanical characteristic. From polyamides to polyimides values of elastic modulus and destructive voltage are growing. This is due to the stringency of the chain macromolecules. In turn, this increase of rigidity of structures chain macromolecules leads to decreasing their opportunities to high values of deformation, which is what we observe (table 3). Table 3 - Mechanical properties of polyamides and polyimides based on 4,4’- diaminothreephenylmethane (film thickness 25 mkm) №/№ Poly mer Visco sity, ηin, dL/g Modulus of elasticity, E, HPa rupture stress, σr, MPa Deforma tion, ε, % I 1 1,2 1,1 125 67 II 2 0,9 1,3 147 39 III 3 1,4 1,5 135 75 IV 1,1 1,8 158 28 1 - isophthalic acid dichlorohydrin - 4,4’- diaminothreephenyl-methane, 2 - terephthalic acid dichlorohydrin - 4,4’- diaminothreephenyl-methane, 3 - diphenylcarbazone acid 4,4’-dichlorohydrin - 4,4’- diaminothreephenyl-methane, 4 - pyromellitic of dianhydride - 4,4’- diaminothreephenyl-methane The results of x-ray analysis of films based on synthetic polyamide and polyimides suggest that all polymers are amorphous. Significant differences in the position and form of amorphous halo in polyimides were observed between the materials prepared by chemical and thermal imidization. A similar effect of imidization method on packaging aromatic polyimides was noted in previous messages for polypyromellitimide based on 4,4’- diaminothreephenylmethane and 4,4’diaminodiphenyl [17]. Conclusion Series of completely aromatic polyamides and polyimides based on 4,4’diaminothreephenylmethane was synthesized and characterized. All studied polymers have good solubility in organic solvents. Solubility of polymer-based on 4,4’-diaminothreephenylmethane, obviously, is connected with the freedom of internal rotation triphenylmethanol bridge group and a surround Deputy in the monomer. Solubility of polyimides based on 4,4’-diaminothreephenylmethane decreases sharply after heat treatment at a temperature 270 0C and above (or samples, which was prepared by thermal imidization), which may be explained by the course of the process of cross-linking of polymers. It is found that studied polymers by thermal and mechanical properties are close to polyamides and polyimides on the basis of other monomers with bridge group.