

Synthesis of New Conjugated Diynes Containing Carbamate Groups, and Study of Their Properties

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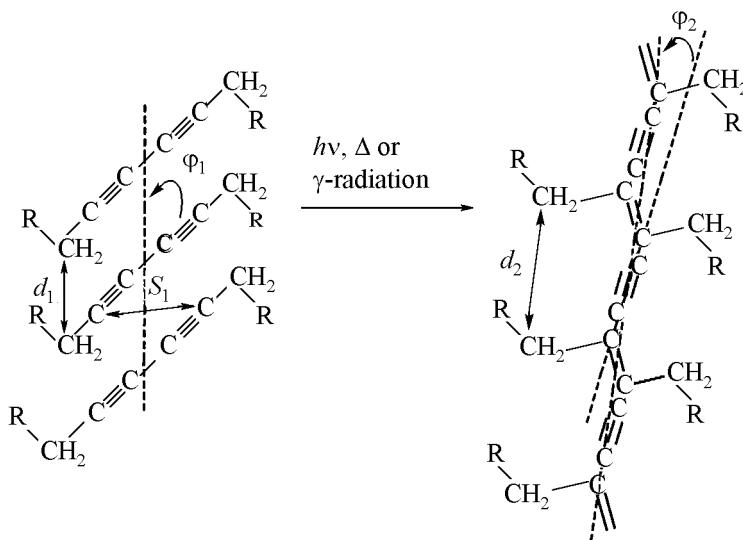
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Abstract—Carbamates of monoacetylene and diacetylene series were synthesized and characterized. A catalytic system CuI-pyrrolidine was applied for the first time to a synthesis of symmetrical diacetylenes by oxidative dimerization of terminal acetylenes. The comparative activity of diynes obtained was studied in the photoinitiated solid-phase topochemical polymerization. Diyne carbamates undergoing thermal polymerization were obtained for the first time.

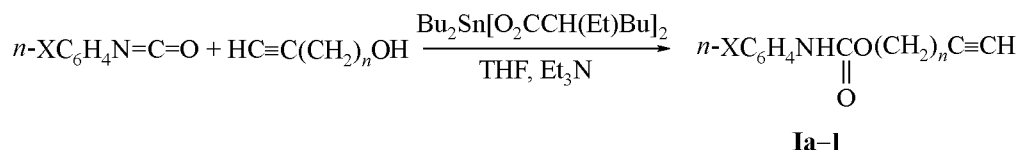
Functionally-substituted diacetylenes are interesting both from theoretical and practical viewpoints, and therefore they are the object of versatile interdisciplinary studies [1]. Diacetylene moiety is encountered in many natural compounds [2], and synthetic antibiotics containing endiynes structure exhibit pronounced anticancer activity [3]. The compounds have found wide use in fine and general organic synthesis [4, 5]. The studies in this field got a new momentum from the discovery of Wegner of solid-phase topochemical polymerization of these compounds initiated by UV and γ -radiation, and sometimes by just heating [6]. Polyacetylenes generated by this process possess unidimensional totally conjugated backbone with mainly enyne (seldom butatriene) crystal structure [7].

The unique feature of the reaction is the possibility to obtain a single crystal of polymer from a single crystal of monomer. The polyacetylenes are more and more applied as chromatic element in biosensors [8-10]. They are especially promising materials for non-linear optics since they possess the largest values of non-linear optical susceptibility of the third order (θ^3) among all known organic compounds [11, 12]. The polymerizability of initial monomeric diynes and polymerization rate essentially depend on the specificity of molecular packing in crystals [13]. The usually applied criteria are taken from crystallography: d_1 , the distance between the neighboring molecules in a stack, and η_1 , the angle between the axis through the system of triple carbon-carbon bonds, and the axis through the centers of the ordinary



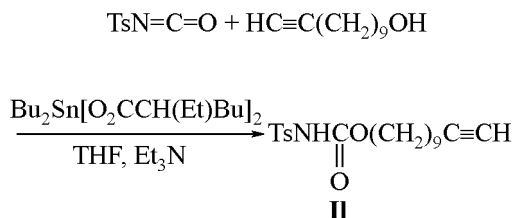
carbon-carbon bonds that are located between the triple bonds. Instead of d_1 parameter S_1 is often used. The values $d_1 \leq 4.9 \text{ \AA}$, $3.4 \text{ \AA} \leq S_1 \leq 4.0 \text{ \AA}$, $\varphi_1 \approx 45^\circ$ are the best, for in this case the reacting carbon atoms are approached to a required distance, and *trans*-1,4-polyaddition occurs. However in a general case the prediction of diacetylene molecule packing in a crystal cannot be performed basing on its structural formula.

The target of this study was establishing of relation between the structure and activity in solid-phase topochemical polymerization of diynes with arylcarbamate groups capable of forming hydrogen bonds in the neighboring stacks and thus of approaching them in space. The other factors affecting the polymerization are the number of methylene groups between the system of the triple bonds and arylcarbamate groups, and the character of substituent in the arylcarbamate group which by its donor or acceptor properties can influence the strength of the hydrogen bond.



X = H (**a, d, h, j, k**), MeO (**b, e**), NO₂ (**c, f**), Me₂N (**g, i**); $n = 2$ (**a-c**), 3 (**d-g**), 6 (**h, i**), 7 (**j**), 9 (**k**).

Compound **II** was prepared by reaction of 10-undecyn-1-ol with tosyl isocyanate along the following scheme:



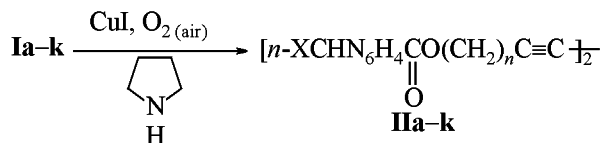
Isocyanates are known to be supersensitive to moisture forming with water the corresponding *N,N'*-diarylcabamides. The monoacetylene carbamates were isolated by preparative TLC. The spectral data confirming the structure of compounds **Ia-l** obtained are presented in Table 1, and physical constants and elemental analyses in Table 2.

Diyne carbamates **IIa-k** were prepared by oxidative dimerization of monoacetylene carbamates **Ia-k**. The oxidative dimerization process of terminal acetylenes has several modifications [15, 16]. We

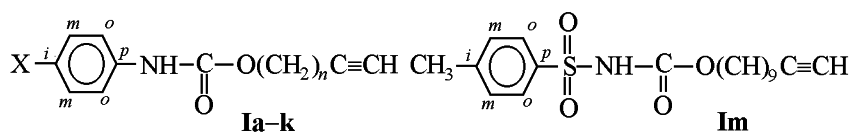
The synthesis of diacetylene arylcarbamates can be effected along two ways. The first one involves a synthesis of monoacetylene terminal arylcarbamates followed by their oxidative dimerization into the target products. The second way includes reaction of diacetylene glycols with aryl isocyanates. The disadvantage of the latter procedure consists in the possibility of side reaction affording cyclic ether by intermolecular dehydration of two molecules of diacetylene glycol effected by aryl isocyanate. For instance, in reaction of dodeca-5,7-diyne-1,12-diol with phenyl isocyanate alongside diacetylene carbamate were obtained carbanilide and a cyclic diacetylene ether formed as a result of dehydration of the initial diacetylene glycol with phenyl isocyanate [14]. Therefore we chose the first method.

The reaction of monoacetylene alcohols and aryl isocyanates gave rise to monoacetylene carbamates **Ia-l**.

were the first to use in the synthesis of symmetrical diynes a catalytic system CuI-pyrrolidine that was formerly successfully applied to preparation of unsymmetrical diynes [17]. It is known from published data that in oxidative dimerization of the terminal acetylenes the choice of a base plays a crucial role [18], and here are important both the basicity and the sterical accessibility of the nitrogen for the interaction with copper salts. Pyrrolidine is a strong base (pK_a 11.1) [19], and it has been applied both as a catalyst and a solvent, and oxidation has been effected by air oxygen.



X = H (**a, d, h, j, k**), MeO (**b, e**), NO₂ (**c, f**), Me₂N (**g, i**); $n = 2$ (**a-c**), 3 (**d-g**), 6 (**h, i**), 7 (**j**), 9 (**k**).

Table 1. IR, ^1H and ^{13}C NMR spectra of monoacetylene carbamates **Ia-l**

Compd. no.	IR spectrum, ν , $\text{cm}^{-1\text{a}}$	^1H NMR spectrum, δ , ppm^{b}	^{13}C NMR spectrum, δ , ppm^{b}
Ia	3445 s(NH), 3340 s(C≡CH), 2110 w (C≡C), 1720 v.s (C=O), 1600 s (C arom-C arom), 1520 s (δ NH)	2.06 t (1H, C≡CH), 2.61 t.d (2H, C≡CCH ₂), 4.28 t (2H, OCH ₂), 6.80 br.s (1H, NH), 7.09 m (1H, <i>p</i> -H arom), 7.40 m (4H, <i>m</i> , <i>o</i> -H arom)	19.74 (C≡CCH ₂), 63.30 (OCH ₂), 70.40 (C≡CH), 80.67 (C≡CH), 119.14 (<i>o</i> -C arom), 124.00 (<i>p</i> -C arom), 129.48 (<i>m</i> -C arom), 138.10 (<i>i</i> -C arom), 153.54 (C=O)
Ib	3445 s (NH), 3320 s (C≡CH), 2110 w C≡C), 1720 v.s (C=O), 1600 s (C arom-C arom), 1510 s (δ NH)	2.05 t (1H, C≡CH), 2.60 t.d (2H, C≡CCH ₂), 3.80 s (3H, OCH ₃), 4.27 t (2H, OCH ₂), 6.70 br.s (1H, NH), 6.69 m (2H, <i>m</i> -H arom), 7.29 m (2H, <i>o</i> -H arom)	19.75 (C≡CCH ₂), 55.90 (OCH ₃), 63.22 (CH ₂ O), 70.33 (C≡CH), 80.72 (C≡CH), 114.67 (<i>m</i> -C arom), 121.18 (<i>o</i> -C arom), 131.13 (<i>i</i> -C arom), 153.92 (C=O), 156.48 (<i>p</i> -C arom)
Ic	3270 s(NH), 3390 s(C≡CH), 3060 s (C arom H), 2950 s (C _{sp³} H), 2930 s (C _{sp³} H), 2110 w (C≡C), 1730 v.s (C=O), 1600 c (C arom-C arom), 1555 v.s (ν_{as} NO ₂), 1510 s (δ NH), 1330 v.s (ν_{s} NO ₂)	2.07 t (1H, C≡CH), 2.62 t.d (2H, C≡CCH ₂), 4.27 t (2H, OCH ₂), 7.80 m (2H, <i>o</i> -H arom), 8.21 m (2H, <i>m</i> -H arom), 9.40 br.s (1H, NH)	19.07 (C≡CCH ₂), 63.51 (CH ₂ O), 70.93 (C≡CH), 80.59 (C≡CCH ₂), 118.16 (<i>o</i> -C arom), 125.22 (<i>m</i> -C arom), 142.95 (<i>i</i> -C arom), 146.02 (<i>p</i> -C arom), 153.38 (C=O)
Id	3280 s (NH), 3305 s (C≡CH), 3040 s (C arom H), 2960 s (C _{sp³} H), 2930 c (C _{sp³} H), 2110 w (C≡C), 1700 v.s (C=O), 1600 s (C arom-C arom), 1545 s (δ NH)	1.90 qn (2H, CH ₂ CH ₂ CH ₂), 2.07 t (1H, C≡CH), 2.34 t.d (2H, C≡CCH ₂), 4.29 t (2H, OCH ₂), 6.90 br.s (1H, NH), 7.05 t (1H, <i>p</i> -H arom), 7.28 t (2H, <i>m</i> -H arom), 7.38 d (2H, <i>o</i> -H arom)	15.57 (C≡CCH ₂), 28.24 (CH ₂ CH ₂ CH ₂), 64.11 (CH ₂ O), 69.55 (C≡CH), 83.45 (C≡CH), 119.17 (<i>o</i> -C arom), 123.84 (<i>p</i> -C arom), 129.43 (<i>m</i> -C arom), 138.31 (<i>i</i> -C arom), 153.98 (C=O)
Ie	3270 s(NH), 3310 s(C≡CH), 3040 s (C arom H), 2960 s (C _{sp³} H), 2940 s (C _{sp³} H), 2860 s (C _{sp³} H), 2110 w (C≡C), 1700 v.s (C=O), 1600 s (C arom-C arom), 1535 s (δ NH)	1.89 qn (2H, CH ₂ CH ₂ CH ₂), 2.01 t (1H, C≡CH), 2.32 t.d (2H, C≡CCH ₂), 3.79 s (3H, OCH ₃), 4.25 t (2H, OCH ₂), 6.79 br.s (1H, NH), 6.85 d (2H, <i>m</i> -H arom), 7.28 d (2H, <i>o</i> -H arom)	15.56 (C≡CCH ₂), 28.28 (CH ₂ CH ₂ CH ₂), 55.88 (OCH ₃), 64.02 (CH ₂ O), 69.50 (C≡CH), 83.51 (C≡CH), 114.64 (<i>m</i> -C arom), 121.17 (<i>o</i> -C arom), 131.35 (<i>i</i> -C arom), 154.37 (C=O), 156.38 (<i>p</i> -C arom)
If	3285 s(NH), 3380 s(C≡CH), 3040 s (C arom H), 2960 s (C _{sp³} H), 2930 s (C _{sp³} H), 2110 w (C≡C), 1730 v.s (C=O), 1600 s (C arom-C arom), 1555 v.s (ν_{as} NO ₂), 1510 s (δ NH), 1330 v.s (ν_{s} NO ₂)	1.89 qn (2H, CH ₂ CH ₂ CH ₂), 2.06 t (1H, C≡CH), 2.32 t.d (2H, C≡CCH ₂), 4.28 t (2H, OCH ₂), 7.75 d (2H, <i>o</i> -H arom), 8.29 d (2H, <i>m</i> -H arom), 9.30 br.s (1H, NH)	14.91 (C≡CCH ₂), 28.13 (CH ₂ CH ₂ CH ₂), 64.12 (CH ₂ O), 70.02 (C≡CH), 83.23 (C≡CH), 118.06 (<i>o</i> -C arom), 125.22 (<i>m</i> -C arom), 142.85 (<i>i</i> -C arom), 145.97 (<i>p</i> -C arom), 154.57 (C=O)
Ig	3440 s (NH), 3310 s(C≡CH), 2110 w (C≡C), 1720 v.s (C=O), 1580 s (C arom-C arom), 1510 s (δ NH)	1.91 qn (2H, CH ₂ CH ₂ CH ₂), 2.01 t (1H, C≡CH), 2.33 t.d (2H, C≡CCH ₂), 2.92 s (6H, CH ₃), 4.25 t (2H, OCH ₂), 6.41 br.s (1H, NH), 6.75 d (2H, <i>m</i> -H arom), 7.21 d (2H, <i>o</i> -H arom)	15.61 (C≡CCH ₂), 28.34 (CH ₂ CH ₂ CH ₂), 41.47 (CH ₃), 63.91 (CH ₂ O), 69.35 (C≡CH), 83.56 (C≡CH), 113.81 (<i>m</i> -C arom), 121.43 (<i>o</i> -C arom), 128.00 (<i>i</i> -C arom), 148.10 (<i>p</i> -C arom), 154.36 (C=O)

Table 1. (Contd.)

Compd. no.	IR spectrum, ν , cm^{-1a}	^1H NMR spectrum, δ , ppm ^b	^{13}C NMR spectrum, δ , ppm ^b
Ih	3440 s(NH), 3315 s(C≡CH), 2120 w (C≡C), 1710 v.s (C=O), 1600 s (C arom-C arom), 1510 s (δ NH)	1.4–1.6 m (6H, CH ₂), 1.70 qn (2H, CH ₂), 1.97 t (1H, C≡CH), 2.21 t. d (2H, C≡CCH ₂), 4.18 t (2H, OCH ₂), 6.79 br.s (1H, NH), 7.07 t (1H, <i>p</i> -H arom), 7.31 t (2H, <i>m</i> -H arom), 7.39 d (2H, <i>o</i> -H arom)	18.72 (C≡CCH ₂), 25.80, 28.19, 28.71, 29.20 (CH ₂), 65.65 (CH ₂ O), 68.74 (C≡CH), 84.91 (C≡CH), 119.09 (<i>o</i> -C arom), 123.74 (<i>p</i> -C arom), 129.42 (<i>m</i> -C arom), 138.40 (<i>i</i> -C arom), 154.16 (C=O)
Ii	3440 s(NH), 3310 s(C≡CH), 2110 w (C≡C), 1720 v.s (C=O), 1580 s (C arom-C arom), 1510 s (δ NH)	1.4–1.6 m (6H, CH ₂), 1.70 qn (2H, CH ₂), 1.98 t (1H, C≡CH), 2.21 t.d (2H, C≡CCH ₂), 2.93 s (6H, CH ₃), 4.15 t (2H, OCH ₂), 6.40 br.s (1H, NH), 6.72 d (2H, <i>m</i> -H arom), 7.21 d (2H, <i>o</i> -H arom)	18.72 (C≡CCH ₂), 25.82, 28.22, 28.73, 29.26, (CH ₂), 41.48 (CH ₃), 65.45 (CH ₂ O), 68.65 (C≡CH), 84.93 (C≡CH), 113.80 (<i>m</i> -C arom), 121.39 (<i>o</i> -C arom), 127.97 (<i>i</i> -C arom), 148.12 (<i>p</i> -C arom), 154.38 (C=O)
Ij	3450 s(NH), 3320 s(C≡CH), 2120 w (C≡C), 1720 v.s (C=O), 1600 s (C arom-C arom), 1510 s (δ NH)	1.3–1.8 m (10H, CH ₂), 1.96 t (1H, C≡CH), 2.21 t.d (2H, C≡CCH ₂), 4.19 t (2H, OCH ₂), 6.67 br.s (1H, NH), 7.08 t (1H, <i>p</i> -H), 7.31 t (2H, <i>m</i> -H arom), 7.39 d (2H, <i>o</i> -H arom)	18.76 (C≡CCH ₂), 26.14, 28.74, 28.97, 29.1, 31.10 (CH ₂), 65.72 (CH ₂ O), 68.59 (C≡CH), 85.03 (C≡CH), 119.05 (<i>o</i> -C arom), 123.74 (<i>p</i> -C arom), 129.43 (<i>m</i> -C arom), 138.37 (<i>i</i> -C arom), 154.07 (C=O)
Ik	3450 s(NH), 3320 s(C≡CH), 2120 w (C≡C), 1720 v.s (C=O), 1600 s (C arom-C arom), 1510 s (δ NH)	1.2–1.8 m (14H, CH ₂), 1.96 t (1H, C≡CH), 2.21 t.d (2H, C≡CCH ₂), 4.19 t (2H, OCH ₂), 6.69 br.s (1H, NH), 7.08 t (1H, <i>p</i> -H arom), 7.31 t (2H, <i>m</i> -H arom), 7.39 d (2H, <i>o</i> -H arom)	18.79 (C≡CCH ₂), 26.24, 28.85, 29.10, 29.33, 29.40, 29.60, 29.76 (CH ₂), 65.79 (CH ₂ O), 68.52 (C≡CH), 85.16 (C≡CH), 119.03 (<i>o</i> -C arom), 123.72 (<i>p</i> -C arom), 129.43 (<i>m</i> -C arom), 138.40 (<i>i</i> -C arom), 154.11 (C=O)
Il	3470 s(NH), 3290 s(C≡CH), 2120 w (C≡C), 1735 v.s (C=O), 1590 s (C arom-C arom), 1340 v.s (ν_{as} SO ₂), 1150 v.s (ν_{s} SO ₂)	1.19–1.45 m (10H, CH ₂), 1.45–1.62 m (4H, CH ₂), 1.96 t (1H, C≡CH), 2.18 t.d (2H, C≡CCH ₂), 2.46 s (3H, CH ₃), 4.06 t (2H, OCH ₂), 7.28 br.s (1H, NH), 7.32 d (2H, <i>m</i> -H arom), 7.92 d (2H, <i>o</i> -H arom)	18.20 (C≡CCH ₂), 21.51, 25.37, 28.24, 28.49, 28.79, 28.87, 29.10 (CH ₂), 67.02 (CH ₃), 67.99 (CH ₂ O), 76.47 (C≡CH), 84.56 (C≡CH), 128.19 (<i>m</i> -C arom), 129.41 (<i>o</i> -C arom), 135.49 (<i>p</i> -C arom), 144.81 (<i>i</i> -C arom), 150.51 (C=O)

^a IR spectra of compounds **Ia**, **b**, **g–l** were recorded in CHCl₃, those of compounds **Ic–f** from KBr pellets.

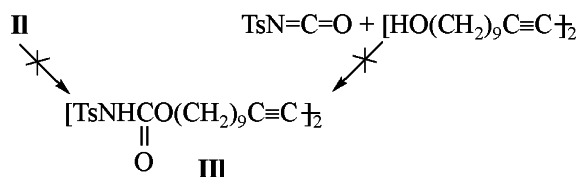
^b ^1H and ^{13}C NMR spectra of compounds **Ic**, **f** were registered in acetone-*d*₆, of the other compounds in CDCl₃.

Table 2. Yields, melting points, and elemental analyses of monoacetylene carbamates **Ia–k**

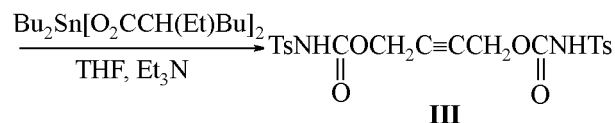
Compd. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Ia	79	52–53	70.04	5.79	7.33	C ₁₁ H ₁₁ NO ₂	69.83	5.86	7.40
Ib	61	84–86	65.78	6.37	6.19	C ₁₂ H ₁₃ NO ₃	65.74	6.44	6.39
Ic	50	118–120	56.32	4.36	11.94	C ₁₁ H ₁₀ N ₂ O ₄	56.41	4.30	11.96
Id	50	45–47	70.90	6.57	6.93	C ₁₂ H ₁₃ NO ₂	70.92	6.45	6.89
Ie	71	46–48	67.25	6.48	5.92	C ₁₃ H ₁₅ NO ₃	66.94	6.48	6.00
If	47	93–94	58.07	5.06	11.03	C ₁₂ H ₁₂ N ₂ O ₄	58.06	4.87	11.29
Ig	44	103–105	68.24	7.37	11.42	C ₁₄ H ₁₈ N ₂ O ₂	68.27	7.37	11.37
Ih	43	46–48	73.25	7.66	5.86	C ₁₅ H ₁₉ NO ₂	73.42	7.80	5.71
Ii	67	70–72	70.94	8.45	9.86	C ₁₇ H ₂₄ N ₂ O ₂	70.80	8.39	9.71
Ij	50	48–49	74.30	8.07	5.50	C ₁₆ H ₂₁ NO ₂	74.10	8.16	5.40
Ik	81	44–46	75.11	9.03	5.08	C ₁₈ H ₂₅ NO ₂	75.22	8.77	4.87
Il	40	70–72	62.17	7.45	3.91	C ₁₉ H ₂₇ NO ₄ S	62.44	7.45	3.83

The reaction was completed within 15–20 min and furnished the desired compounds in high yield. The products were isolated from the reaction mixture as follows. First the reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with tetrahydrofuran. The diacetylene compound after removing THF contained pyrrolidine as an impurity. Further purification was carried out by two procedures: by chromatography and by treating the diacetylene on glass frit filter with diluted hydrochloric acid. The attempts to separate this mixture by preparative thin-layer chromatography were inefficient for diynes easily polymerized on the sorbent hampering the elution. This fact resulted in a relatively low yield (48%) of compound **IIa**. The washing of diynes with 15% aqueous HCl was more successful. We also demonstrated that this method provided excellent results also in dimerization of terminal acetylene alcohols. We attempted to carry out the dimerization of terminal acetylenes by classical method with Glaser–Hay catalyst (complex of CuCl with tetramethylethylenediamine) and oxygen flow through the reaction mixture for several hours to effect oxidation. However this attempt failed even at equimolar amounts of the catalyst and terminal acetylene.

We tried to prepare from compound **II** the corresponding diyne by oxidative dimerization on catalytic systems CuI –pyrrolidine, CuI – i - Pr_2NH – $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ – I_2 [20], and also by Hay [21, 22] and Eglintone methods [23]. At the use of two former systems strong tarring occurred, and after using Glaser–Hay or Eglintone procedures the initial tosyl carbamate **II** remained intact and was recovered from the reaction mixture. In special runs compound **II** was stirred with equimolar amounts of CuI dispersion both in pyrrolidine and dichloromethane solution, and the initial tosyl carbamate did not suffer any changes. The reaction of 10,12-docosadiyne-1,22-diol and tosyl isocyanate provided a complex mixture of products, and we failed to isolate from the mixture the desired diyne.



Yet the reaction of 2-butyne-1,4-diol with tosyl isocyanate under conditions used in the synthesis of monoacetylene carbamates **Ia–I** afforded product **III**; its structure and composition was proved by spectral data and elemental analysis.



We cannot yet rationalize the different behavior pattern of acetylene and diacetylene diols in reaction with tosyl isocyanate.

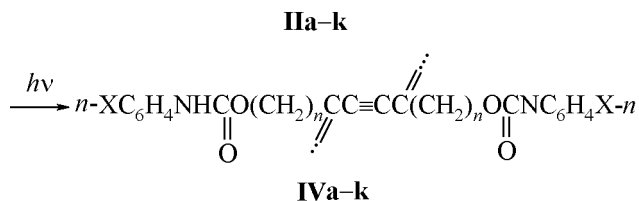
We carried out estimation of the strength of intermolecular hydrogen bond in solid compound **IIId**. To this end the IR spectra of the compound were registered from a sample pelleted with KBr and from solutions in CH_2Cl_2 of 1% and 0.5% concentration. Therewith the absorption band of the stretching vibrations of the N–H bond appeared in the first case at 3333 cm^{-1} whereas in both solutions this band was observed at 3430 cm^{-1} . The formation enthalpy of the hydrogen bond may be calculated by a formula from [24].

$$-\Delta H = 1.3 (\Delta\nu)^{1/2},$$

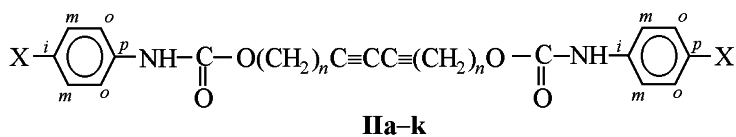
where ΔH is formation enthalpy of the hydrogen bond (kJ mol^{-1}), $\Delta\nu$ is the frequency difference for the stretching vibrations ν_{NH} in diluted solution and in the solid state respectively (cm^{-1}). Our calculation gave the value -12.8 kJ mol^{-1} . It should be noted however that the formation enthalpy value for a hydrogen bond is considered to be appropriate if the $\Delta\nu$ is larger than 100 cm^{-1} [25]; in our case this value amounted to 93 cm^{-1} .

The spectral data supporting the structure of compounds **IIa–k** obtained are listed in Table 3, physical constants and elemental analyses in Table 4.

The final stage of this study involved investigation of photoinitiated polymerization of diyne carbamates **IIa–k** in the solid phase under UV light with various wavelength [26].



It is known from published data that whereas the activation energy of thermal polymerization amounts to $80\text{--}105\text{ kJ mol}^{-1}$, the corresponding value for photopolymerization reaches only 10 kJ mol^{-1} [27]. To the polymerization kinetics correspond two types of curves: with a long induction time and with none [28, 29].

Table 3. IR, ^1H and ^{13}C NMR spectra of diacetylene carbamates **IIa-k**

Compd. no.	IR spectrum, ν , cm^{-1a}	^1H NMR spectrum, δ , ppm ^b	^{13}C NMR spectrum, δ , ppm ^b
IIa	3445 s(NH), 1740 v.s (C=O), 1600 s (C arom-C arom), 1520 s (δ NH)	2.68 t(4H, C≡CCH ₂), 4.21 t (4H, OCH ₂), 7.01 t (2H, <i>p</i> -H arom), 7.30 t (4H, <i>m</i> -H arom), 7.60 d (4H, <i>o</i> -H arom), 8.79 br.s (2H, NH)	19.91 (C≡CCH ₂), 62.44 (OCH ₂), 66.49 (C≡CC≡C), 74.74 (CH ₂ C≡C), 118.71 (<i>o</i> -C arom), 123.06 (<i>p</i> -C arom), 129.13 (<i>m</i> -C arom), 139.58 (<i>i</i> -C arom), 153.58 (C=O)
IIb	3450 s(NH), 1720 v.s (C=O), 1600 s (C arom-C arom), 1520 s (δ NH)	2.69 t (4H, C≡CCH ₂), 3.79 s(6H, OCH ₃), 4.21 t (4H, OCH ₂), 6.87 d (4H, <i>m</i> -H arom), 7.49 d (4H, <i>o</i> -H arom), 8.61 br.s (2H, NH)	19.57 (C≡CCH ₂), 55.14 (OCH ₃), 62.32 (OCH ₂), 68.02 (C≡CC≡C), 74.48 (CH ₂ C≡C), 114.29 (<i>m</i> -C arom), 121.15 (<i>o</i> -C arom), 131.38 (<i>i</i> -C arom), 154.37 (C=O), 156.38 (<i>p</i> -C arom)
IIc	3330 s(NH), 3060 s(C arom H), 3040 s(C arom H), 2960 s (C _{sp³} H), 2850 s(C _{sp³} H), 1740 v.s (C=O), 1600 s(C arom-C arom), 1555 v.s (v _{as} NO ₂), 1520 s(δ NH), 1330 v.s (v _s NO ₂)	2.77 t(4H, C≡CCH ₂), 4.21 t(4H, OCH ₂), 7.82 d (4H, <i>o</i> -H arom), 8.22 d (4H, <i>m</i> -H arom), 9.50 br.s (2H, NH)	19.77 (C≡CCH ₂), 63.10 (OCH ₂), 66.20 (C≡CC≡C), 74.42 (CH ₂ C≡C), 118.22 (<i>o</i> -C arom), 1125.25 (<i>m</i> -C arom), 142.42 (<i>i</i> -C arom), 146.02 (<i>p</i> -C arom), 153.50 (C=O)
IId	3330 s(NH), 3050 s(C arom H), 3040 s(C arom H), 2950 s (C _{sp³} H), 2840 s(C _{sp³} H), 1700 v.s (C=O), 1600 s(C arom-C arom), 1535 s (δ NH)	1.89 qn (4H, CH ₂ CH ₂ CH ₂), 2.40 t (4H, C≡CCH ₂), 4.20 t (4H, OCH ₂), 7.00 t (2H, <i>p</i> -H arom), 7.27 t (4H, <i>m</i> -H arom), 8.55 d (4H, <i>o</i> -H arom), 8.67 br.s (2H, NH)	15.68 (C≡CCH ₂), 28.10 (CH ₂ CH ₂ CH ₂), 63.31 (CH ₂ O), 66.02 (C≡CC≡C), 76.80 (C≡CCH ₂), 118.64 (<i>o</i> -C arom), 122.91 (<i>p</i> -C arom), 129.10 (<i>m</i> -C arom), 139.74 (<i>i</i> -C arom), 153.85 (C=O)
IIe	3300 s(NH), 3040 s(C arom H), 2960 s(C _{sp³} H), 2930 s (C _{sp³} H), 2830 s(C _{sp³} H), 1700 v.s (C=O), 1600 s (C arom-C arom), 1515 © (δ NH)	1.89 qn (4H, CH ₂ CH ₂ CH ₂), 2.41 t (4H, C≡CCH ₂), 3.79 s(6H, OCH ₃), 4.18 t (4H, OCH ₂), 6.67 d (4H, <i>m</i> -H arom), 7.47 d (4H, <i>o</i> -H arom), 8.48 br.s (2H, NH)	14.93 (C≡CCH ₂), 27.39 (CH ₂ CH ₂ CH ₂), 54.38 (OCH ₃), 62.42 (CH ₂ O), 65.24 (C≡CC≡C), 76.06 (C≡CCH ₂), 113.51 (<i>m</i> -C arom), 119.53 (<i>o</i> -C arom), 132.00 (<i>i</i> -C arom), 153.29 (C=O), 156.16 (<i>p</i> -C arom)
IIf	3300 s (NH), 3040 s (C arom H), 2930 © (C _{sp³} H), 2860 c (C _{sp³} H), 1740 v.s (C=O), 1600 c (C arom-C arom), 1555 v.s (v _{as} NO ₂), 1510 © (δ NH), 1330 v.s (v _s NO ₂)	1.89 qn (4H, CH ₂ CH ₂ CH ₂), 2.42 t (4H, C≡CCH ₂), 4.25 t (4H, OCH ₂), 7.89 d (4H, <i>o</i> -H arom), 8.21 d (4H, <i>m</i> -H arom), 9.28 br.s (2H, NH)	15.65 (C≡CCH ₂), 27.89 (CH ₂ CH ₂ CH ₂), 62.42 (CH ₂ O), 66.04 (C≡CC≡C), 76.72 (C≡CCH ₂), 118.12 (<i>o</i> -C arom), 119.53 (<i>m</i> -C arom), 142.89 (<i>i</i> -C arom), 145.98 (<i>p</i> -C arom), 153.56 (C=O)
IIg	3300 s(NH), 3040 s(C arom H), 2960 s(C _{sp³} H), 2850 s (C _{sp³} H), 1690 v.s (C=O), 1610 s(C arom-C arom), 1515 s (δ NH)	1.89 qn (4H, CH ₂ CH ₂ CH ₂), 2.42 t (4H, C≡CCH ₂), 2.92 s(12H, NMe ₂), 4.22 t (4H, OCH ₂), 6.42 br.s (2H, NH), 6.72 d (4H, <i>m</i> -H arom), 7.21 d (4H, <i>o</i> -H arom)	16.49 (C≡CCH ₂), 28.23 (CH ₂ CH ₂ CH ₂), 41.42 (CH ₃), 63.93 (CH ₂ O), 66.27 (C≡CC≡C), 113.74 (<i>m</i> -C arom), 121.74 (<i>o</i> -C arom), 128.02 (<i>i</i> -C arom), 148.10 (<i>p</i> -C arom), 154.32 (C=O)

Table 3. (Contd.)

Compd. no.	IR spectrum, ν , cm^{-1a}	^1H NMR spectrum, δ , ppm ^b	^{13}C NMR spectrum, δ , ppm ^b
IIh	3480 s(NH), 1750 v.s (C=O), 1600 s(C arom-C arom), 1505 s (δ NH)	1.31–1.75 m (16H, CH_2), 2.28 t (4H, $\text{C}\equiv\text{CCH}_2$), 4.20 t (4H, OCH_2), 6.68 br.s (2H, NH), 7.08 t (2H, <i>p</i> -H arom), 7.31 t (4H, <i>m</i> -H arom), 7.39 d (4H, <i>o</i> -H arom)	19.52 ($\text{C}\equiv\text{CCH}_2$), 25.81, 28.53, 28.81, 29.17 (CH_2), 65.64 (CH_2O), 65.84 ($\text{C}\equiv\text{CC}\equiv\text{C}$), 119.05 (<i>o</i> -C arom), 123.76 (<i>p</i> -C arom), 129.44 (<i>m</i> -C arom), 138.36 (<i>i</i> -C arom), 154.07 (C=O)
IIi	3440 s(NH), 1720 v.s (C=O), 1580 s(C arom-C arom), 1510 \odot (δ NH)	1.35–1.75 m (16H, CH_2), 2.37 t (4H, $\text{C}\equiv\text{CCH}_2$), 2.91 s (12H, CH_3), 4.15 t (4H, OCH_2), 6.42 br.s (2H, NH), 6.72 d (4H, <i>m</i> -H arom), 7.21 d (4H, <i>o</i> -H arom)	19.52 ($\text{C}\equiv\text{CCH}_2$), 25.83, 28.56, 28.85, 29.24 (CH_2), 41.46 (CH_3), 65.45 (CH_2O), 65.81 ($\text{C}\equiv\text{CC}\equiv\text{C}$), 113.78 (<i>m</i> -C arom), 121.39 (<i>o</i> -C arom), 128.01 (<i>i</i> -C arom), 148.10 (<i>p</i> -C arom), 154.36 (C=O)
IIj	3440 s(NH), 1720 v.s (C=O), 1600 s(C arom-C arom), 1510 s (δ NH)	1.3–1.75 m (20H, CH_2), 2.28 t (4H, $\text{C}\equiv\text{CCH}_2$), 4.18 t (4H, OCH_2), 6.65 br.s (2H, NH), 7.08 t (2H, <i>p</i> -H arom), 7.30 t (4H, <i>m</i> -H arom), 7.41 d (4H, <i>o</i> -H arom)	19.52 ($\text{C}\equiv\text{CCH}_2$), 26.13, 28.59, 29.08, 29.26, 30.10 (CH_2), 65.70 (CH_2O), 68.36 ($\text{C}\equiv\text{CC}\equiv\text{C}$), 119.06 (<i>o</i> -C arom), 123.73 (<i>p</i> -C arom), 129.42 (<i>m</i> -C arom), 138.39 (<i>i</i> -C arom), 154.09 (C=O)
IIk	3450 s(NH), 1730 v.s (C=O), 1600 s(C arom-C arom), 1510 s (δ NH)	1.2–1.8 m (28H, CH_2), 2.26 t (4H, $\text{C}\equiv\text{CCH}_2$), 4.18 t (4H, OCH_2), 6.67 br.s (2H, NH), 7.07 t (2H, <i>p</i> -H arom), 7.29 t (4H, <i>m</i> -H arom), 7.41 d (4H, <i>o</i> -H arom)	19.60 ($\text{C}\equiv\text{CCH}_2$), 26.24, 28.70, 29.18, 29.33, 29.59, 29.73, 30.11 (CH_2), 65.79 (CH_2O), 68.35 ($\text{C}\equiv\text{CC}\equiv\text{C}$), 119.03 (<i>o</i> -C arom), 123.72 (<i>p</i> -C arom), 129.43 (<i>m</i> -C arom), 138.40 (<i>i</i> -C arom), 154.12 (C=O)

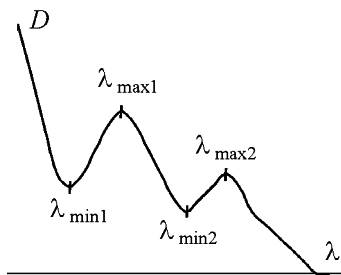
^a IR spectra of compounds **IIa**, **b**, **h–k** were taken in CHCl_3 , of compounds **IIc–g** in KBr pellets.

^b ^1H and ^{13}C NMR spectra of compounds **IIa–f** were recorded in acetone- d_6 , of the other substances in CDCl_3 .

Table 4. Yields, melting points, and elemental analyses of diacetylene carbamates **IIa–k**

Compd. no.	Yield, %	mp, $^\circ\text{C}$	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	48	152–154	70.35	5.67	7.08	$\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4$	70.20	5.36	7.44
IIb	77	^a	66.15	5.67	6.49	$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6$	66.05	5.54	6.42
IIc	90	^a	56.65	3.96	12.21	$\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_8$	56.66	3.89	12.01
IId	77	107–109	71.27	5.91	6.84	$\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4$	71.27	5.98	6.93
IIe	78	129–131	67.46	6.22	6.11	$\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_6$	67.23	6.08	6.03
IIf	90	142–144	58.42	4.32	11.32	$\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_8$	58.30	4.48	11.33
IIg	80	167–169	68.48	6.92	11.41	$\text{C}_{28}\text{H}_{34}\text{N}_4\text{O}_4$	68.55	6.99	11.42
IIh	70	127–129	73.75	7.43	5.72	$\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_4$	73.74	7.43	5.73
IIi	76	160–162	71.16	7.92	9.71	$\text{C}_{34}\text{H}_{46}\text{N}_4\text{O}_4$	71.05	8.07	9.75
IIj	73	118–120	74.03	7.78	5.53	$\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_4$	74.39	7.80	5.42
IIk	89	96–98	75.43	8.44	4.75	$\text{C}_{36}\text{H}_{48}\text{N}_2\text{O}_4$	75.49	8.45	4.89

^a Compounds **IIa**, **b** undergo solid-phase topochemical polymerization before they are heated to melting points.



Typical UV spectrum of diyne carbamates **IIa-k**.

Since the penetrability of the far UV radiation (180–300 nm) is low, the polymerization was carried out in a water dispersion of crushed diyne crystals under stirring. The process is heat-releasing, and therefore water played the role of heat-transfer agent. The irradiation period and wavelength of the UV light were important parameters for the polymerization process.

The results of photoinitiated solid-phase polymerization of compounds **IIa-k** are presented in Table 5. The data suggest the following conclusions. In the series of phenylcarbamates with an odd number of methylene groups ($n = 3, 7, 9$) the activity in polymerization grew with chain elongation. The same effect is observed with phenylcarbamates with an even number of methylene groups ($n = 2, 6$), and the compounds with the even number of methylene groups were more active, than those with the odd number (carbamates with two and six CH_2 groups were more active than their respective analogs with three and seven CH_2 groups). The increase in activity of diyne carbamates with growing number of methylene groups suggested the following hypothesis. It is known that diacetylene molecules located in stacks as bars are synchronously rotating in the course of polymerization without displacement of the mass centers. Since these carbamate molecules are fixed at the ends with the hydrogen bonds this rotation requires internal freedom that is just provided by methylene groups playing the role of spacers. With growing number of methylene groups the degree of freedom also increases resulting in higher polymerization degree. The separation of the diyne carbamates in two groups may be only due to the different crystallographic packing. Interestingly enough that in the literature was described the polymerization of diyne phenylcarbamates with $n = 4, 5, 6$ under γ -irradiation (60 Mrad) where the diyne phenylcarbamate with 5 methylene groups was inactive, and the compounds with 4 and 6 methylene groups furnished polymer in 95 and 70% yield respectively [30].

The data in Table 5 also show that the activity of diyne carbamates in polymerization depends on the wavelength of the radiation. At the use of the mercury lamp of medium pressure PRK-400 with a Pyrex glass filter the samples are irradiated with light in the range of 360–370 nm wavelength. The diyne carbamates have no absorption bands in this spectral range (see figure and Table 6), and therefore no polymerization occurs.

When the same lamp is used without the Pyrex filter, about 16% of the radiation power correspond to the region with a maximum at 254 nm [31] that apparently ensures the activity of diyne arylcarbamates in the solid-phase polymerization. Note however that monomer conversion in this case constitutes about a half of that obtained under irradiation with a lamp BUV-15 with the main wavelength λ_{max} 254 nm. Diyne *p*-nitrophenylcarbamates virtually did not polymerize within the experiment period under UV irradiation with the above sources. However at prolonged (within several tens of hours) standing in diffused daylight a polymerization was observed that apparently should be described with kinetic curves with a long induction period. Although these compounds absorb light at 360–370 nm the intensity is not sufficient for fast polymerization, or the energy of the triplet excited state of the nitrophenylcarbamate group is lower than that of diacetylene group and therefore the energy transfer to the diacetylene fragment becomes impossible.

In a series of diyne carbamates with *para*-substituents in the benzene ring (NO_2 , H, CH_3 , Me_2N) the lowest polymerization activity was observed in *p*-nitrophenylcarbamates **IIb** and **IIe**. The activity considerably grew in going to phenylcarbamates and further to *p*-methoxycarbamate **IIb** and **IIf**. On the contrary, the introduction of a *p*-dimethylamino group (compounds **IIg** and **IIi**) resulted in decreased activity in photopolymerization.

More detailed interpretation of the results obtained requires data on the packing of molecules of these compounds in the unit cells of their crystals.

As reported in the literature [32], the diyne carbamate are not capable of thermal polymerization. The results of this study invalidate this statement. Two among eleven previously unknown diyne carbamates we synthesized were active in thermal polymerization: 3,5-octadiyne-1,8-diyl bis[*n*-(4-methoxyphenyl)carbamate] (**IIb**), and 3,5-octadiyne-1,8-diyl bis[*n*-(4-nitrophenyl)carbamate] (**IIc**). Diyne **IIb** changed from colorless to dark-red even at

Table 5. Degree of diyne carbamate **IIa-k** conversion at UV irradiation from different sources (%)^a

Compd. no.	Lamp BUV-15		Lamp PRK-400 without filter		Color of polymer IVa-k
	run no. 1	run no. 2	run no. 1	run no. 2	
IIa	25	26	–	–	Orange
IIb	80	82	41	42	Dark-red
IIc	0	0	0	0	–
II d	17	17	8	9	Blue
IIe	28	27	14	13	Blue
II f	0	0	0	0	–
II g	9	8	–	–	Light-violet
II h	48	50	–	–	Light-red
II i	28	27	–	–	Dark-red
II j	31	34	–	–	Blue
II k	57	55	27	28	Blue

^a The degree of conversion is given to the nearest percent.

Table 6. UV spectra of diyne carbamates **IIa-k** depending on substituent X in phenyl ring^a

X	$\lambda_{\min} 1$, nm [log $\epsilon_{\min} 1$, l mol ⁻¹ cm ⁻¹]	$\lambda_{\max} 1$, nm [log $\epsilon_{\max} 1$, l mol ⁻¹ cm ⁻¹]	$\lambda_{\min} 2$, nm [log $\epsilon_{\min} 2$, l mol ⁻¹ cm ⁻¹]	$\lambda_{\max} 2$, nm [log $\epsilon_{\max} 2$, l mol ⁻¹ cm ⁻¹]	$\lambda_{250-260}$, nm [log ϵ , l mol ⁻¹ cm ⁻¹]	$\lambda_{360-370}$, nm [log ϵ , l mol ⁻¹ cm ⁻¹]
H	214 (3.84)	235 (4.48)	–	273 (3.27)	250 (3.44) 254 (3.16) 260 (3.13)	360 (–) 366 (–) 370 (–)
MeO	215 (3.79)	240 (4.52)	264 (2.81)	289 (3.49)	250 (4.26) 254 (3.96) 260 (3.01)	360 (–) 366 (–) 370 (–)
NO ₂	210 (4.17)	219 (4.25)	255 (3.37)	319 (4.41)	250 (3.46) 254 (3.37) 260 (3.46)	360 (3.71) 366 (3.53) 370 (3.36)
Me ₂ N	230 (3.82)	266 (4.54)	297 (2.50)	312 (3.54)	250 (4.29) 254 (4.37) 260 (4.49)	360 (–) 366 (–) 370 (–)

^a Average values in homologous series.

storage in a refrigerator. The attempt to measure the melting points of these carbamates led to polymerization, and melting started over 190–200°C with decomposition (with charring and gas evolution).

The structure of polydiacetylenes **IVb**, **IVc**, and **IVi** was proved by Raman spectroscopy. In the spectra of these compounds were present the absorption bands of conjugated double bonds at 1475 (**IVb**), 1480 (**IVc**), 1500 (**IVi**) cm⁻¹, and of conjugated triple bonds at 2100 cm⁻¹ (in all the three compounds). These data exclude the presence of a butatriene structure and reveal formation of polydiacetylenes of

enyne structure. As known from the literature, the absorption bands of triple bonds in the spectra of the initial diacetylenes are situated in the region of higher frequencies. The monomers possess a strong band C≡C at 2260 cm⁻¹, and polymers have two strong bands C≡C at 2100 cm⁻¹, and a C=C band at 1500 cm⁻¹ [33].

EXPERIMENTAL

IR spectra were recorded from 3% solutions in CHCl₃ on spectrophotometer Specord 75IR, from 0.5% and 1% solutions in CH₂Cl₂ and from KBr

pellets on Fourier spectrometer Bruker IFS-88. The Raman spectra were measured on Ramalog-5 instrument equipped with an argon laser (λ 488 nm). UV spectra were taken in CH_3CN on spectrophotometer Specord M40 UV-Vis. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-300 at 300 and 75 MHz respectively, solvents CDCl_3 and $(\text{CD}_3)_2\text{CO}$, internal reference TMS. Mass spectra were obtained on GC-MS instrument MKh-1330, ionizing electrons energy 70 eV. TLC analyses were carried out on Silufol UV-254 plates, development under UV-irradiation or with potassium permanganate solution. The preparative TLC was performed on Silpearl silica gel, spots were visualized under UV irradiation. The topochemical solid-phase polymerization was carried out under UV radiation of mercury lamps of low pressure BUV-15 (λ_{max} 254 nm) and of medium pressure PRK-400 (λ_{max} 366 nm) with and without a Pyrex glass filter.

The initial acetylene alcohols were prepared by the following procedures. 3-Butyn-1-ol was obtained from lithium acetylide and oxirane [34]. 4-Pentyn-1-ol was synthesized by reaction of tetrahydrofurfuryl chloride with sodium amide in liquid ammonia [35]. The synthesis of 6-octyn-1-ol was analogous to [36] and included four stages starting with 1,6-hexanediol. 7-Nonyn-1-ol was prepared by alkylating propargyl alcohol followed by isomerization into a terminal acetylene alcohol [37, 38]. The four-stage synthesis of 10-undecyn-1-ol proceeded from 10-udecenoic acid [39–41].

3-Butyn-1-yl *N*-phenylcarbamate (Ia). To a solution of 1.4 g (20 mmol) of 3-butyn-1-ol, 100 mg of dibutyltin bis(2-ethylhexanoate), and 2 drops of Et_3N in 60 ml of anhydrous THF was added dropwise at stirring 2.98 g (25 mmol) of phenyl isocyanate. Then the reaction mixture was stirred for 1 h (TLC monitoring). After total consumption of the initial 3-butyn-1-ol the solvent was distilled off in a vacuum, and the residue was subjected to preparative TLC on silica gel (eluent hexane–ether, 1:1). The reaction product was eluted from silica gel with THF, and the solution was dried on MgSO_4 .

3-Butyn-1-yl *N*-(4-methoxyphenyl)carbamate (Ib) was prepared similarly to compound **Ia** from 1.05 g (15 mmol) of 3-butyn-1-ol, 2.8 g (18.75 mmol) of 4-methoxyphenyl isocyanate, 75 mg of dibutyltin bis(2-ethylhexanoate), 2 drops of Et_3N , and 45 ml of anhydrous THF.

3-Butyn-1-yl *N*-(4-nitrophenyl)carbamate (Ic) was prepared similarly to compound **Ia** from 1.05 g

(15 mmol) of 3-butyn-1-ol, 3.075 g (18.75 mmol) of 4-nitrophenyl isocyanate, 75 mg of dibutyltin bis(2-ethylhexanoate), 2 drops of Et_3N , and 45 ml of anhydrous THF. The 4-nitrophenyl isocyanate was added by small portions.

4-Pentyn-1-yl *N*-phenylcarbamate (Id) was prepared similarly to compound **Ia** from 0.84 g (10 mmol) of 4-pentyn-1-ol, 1.49 g (12.5 mmol) of phenyl isocyanate, 50 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et_3N , and 30 ml of anhydrous THF.

4-Pentyn-1-yl *N*-(4-methoxyphenyl)carbamate (Ie) was prepared similarly to compound **Ia** from 0.84 g (10 mmol) of 4-pentyn-1-ol, 1.86 g (12.5 mmol) of 4-methoxyphenyl isocyanate, 50 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et_3N , and 30 ml of anhydrous THF.

4-Pentyn-1-yl *N*-(4-nitrophenyl)carbamate (If) was prepared similarly to compound **Ia** from 0.84 g (10 mmol) of 4-pentyn-1-ol, 2.05 g (12.5 mmol) of 4-nitrophenyl isocyanate, 50 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et_3N , and 30 ml of anhydrous THF. The 4-nitrophenyl isocyanate was added by small portions.

4-Pentyn-1-yl *N*-(4-dimethylaminophenyl)carbamate (Ig). To a solution of 0.155 g (1.85 mmol) of 4-pentyn-1-ol dried with molecular sieves, 10 mg of dibutyltin bis(2-ethylhexanoate), and 1 drop of Et_3N in 10 ml of anhydrous THF was added dropwise at stirring 0.32 g (2 mmol) of phenyl isocyanate. The completion of reaction could not be determined by TLC following the consumption of the initial alcohol, for the alcohol and carbamate had the same R_f value. The reaction mixture was stirred for 2 h, the solvent was distilled off in a vacuum, and the residue was subjected to preparative TLC on silica gel (eluent hexane–ether, 5:7). The target product was eluted from silica gel with THF and dried on MgSO_4 .

7-Octyn-1-yl *N*-phenylcarbamate (Ih) was prepared in the same way as compound **Ia** from 0.42 g (3.3 mmol) of 7-octyl-1-ol dried with molecular sieves, 0.43 g (3.63 mmol) of phenyl isocyanate, 15 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et_3N , and 10 ml of anhydrous THF.

7-Octyn-1-yl *N*-(4-dimethylaminophenyl)carbamate (Ii) was prepared in the same way as compound **Ig** from 0.19 g (1.5 mmol) of 7-octyl-1-ol dried with molecular sieves, 0.27 g (1.65 mmol) of 4-dimethylaminophenyl isocyanate, 8 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et_3N , and 10 ml of anhydrous THF.

8-Nonyn-1-yl *N*-phenylcarbamate (Ij) was prepared in the same way as compound **Ia** from 0.42 g (3 mmol) of 8-nonyl-1-ol, 0.445 g (3.75 mmol) of phenyl isocyanate, 15 mg of dibutyltin bis(2-ethylhexanoate), 1 drop of Et₃N, and 10 ml of anhydrous THF.

10-Undecyn-1-yl *N*-phenylcarbamate (Ik) was prepared in the same way as compound **Ia** from 0.84 g (5 mmol) of 10-undecyl-1-ol, 0.715 g (6 mmol) of phenyl isocyanate, 25 mg of dibutyltin bis(2-ethylhexanoate), 2 drops of Et₃N, and 15 ml of anhydrous THF.

10-Undecyn-1-yl *N*-(4-methylphenyl)carbamate (Il) was prepared in the same way as compound **Ia** from 0.84 g (5 mmol) of 10-undecyl-1-ol, 0.76 g (5 mmol) of tosyl isocyanate, 25 mg of dibutyltin bis(2-ethylhexanoate), 2 drops of Et₃N, and 5 ml of anhydrous THF. Mass spectrum, *m/z* (*I*_{rel}, %): 365 (0.5) [*M*]⁺, 302 (1.3) [*M*-SO₂+1]⁺, 301 (5.8) [*M*-SO₂]⁺, 216 (7.8) [TsNHC(OH)₂]⁺, 210 (1.3) [NHC(O)O(CH₂)₉C≡CH]⁺, 199 (0.4) [TsNHC=O]⁺, 198 (1.3) [TsNHC=O]⁺, 197 (3.8) [TsN=C=O]⁺, 156 (2.9) [*p*-CH₃C₆H₄S(O)OH]⁺, 155 (53) [Ts]⁺, 152 (1.0) [CH₃(CH₂)₈C≡CH]⁺, 151 (3.4) [(CH₂)₉C≡CH]⁺, 150 (6.6) [CH₂=CH(CH₂)₇C≡CH]⁺, 135 (4.2), 122 (0.8) [CH₃(CH₂)₆C≡CH]⁺, 121 (7.0) [(CH₂)₇C≡CH]⁺, 120 (7.6) [CH₂=CH(CH₂)₅C≡CH]⁺, 110 (3.1) [CH₃(CH₂)₅C≡CH]⁺, 109 (10) [(CH₂)₆C≡CH]⁺, 108 (78) [CH₂=CH(CH₂)₄C≡CH]⁺, 107 (18) [CH₂=CHCH(CH₂)₃C≡CH]⁺, 91 (100) [CH₃C₆H₅]⁺, 82 (32) [CH₃(CH₂)₃C≡CH]⁺, 81 (14) [(CH₂)₄C≡CH]⁺, 80 (26) [CH₂=CH(CH₂)₂C≡CH]⁺, 69 (26) [CH₃(CH₂)₂C≡CH]⁺, 68 (37) [CH₃(CH₂)₂C≡CH]⁺, 67 (5) [(CH₂)₃C≡CH]⁺, 66 (26) [CH₂=CHCH₂C≡CH]⁺, 55 (32) [CH₃CH₂C≡CH]⁺, 54 (18) [CH₃CH₂C≡CH]⁺, 41 (55) [CH₃C≡CH]⁺, 39 (18) [CH₂C≡CH]⁺.

3,5-Octadiyne-1,8-diyl bis-*N*-phenylcarbamate (IIa). In 3 ml of pyrrolidine was dissolved 0.45 g (2.28 mmol) of carbamate **Ia** and 44 mg (0.23 mmol) of CuI. The reaction mixture was stirred at room temperature for 20 min. At this moment TLC test showed no initial compound in the reaction mixture. Then the reaction mixture was quenched with saturated aqueous NH₄Cl (5 ml), and extracted with THF (3×10 ml). THF was distilled off in a vacuum, the reaction product was isolated by preparative TLC on silica gel (eluent ether-THF, 10:1). The target product was washed from silica gel with THF and

dried on MgSO₄. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 235 (4.79), 273 (3.28) fine structure.

3,5-Octadiyne-1,8-diyl bis-*N*-(4-methoxyphenyl)carbamate (IIb). In 1.5 ml of pyrrolidine was dissolved 0.22 g (1 mmol) of carbamate **Ib** and 19 mg (0.1 mmol) of CuI. The reaction mixture was stirred at room temperature for 15 min. Then the reaction mixture was quenched with saturated aqueous NH₄Cl (5 ml), and extracted with THF (3×10 ml). After THF was distilled off in a vacuum, the residue was washed with 15% water solution of HCl and then with water till neutral washings. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 240 (4.51), 289 (3.49).

3,5-Octadiyne-1,8-diyl bis-*N*-(4-nitrophenyl)carbamate (IIc) was prepared analogously to compound **IIb** from 0.235 g (1 mmol) of carbamate **Ic**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 218 (4.23), 318 (4.38).

4,6-Decadiyne-1,10-diyl bis-*N*-phenylcarbamate (IId) was prepared analogously to compound **IIb** from 0.406 g (2 mmol) of carbamate **Id**, 38 mg (0.2 mmol) of CuI, and 2 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 235 (4.54), 273 (3.15) fine structure.

4,6-Decadiyne-1,10-diyl bis-*N*-(4-methoxyphenyl)carbamate (IIe) was prepared analogously to compound **IIb** from 0.23 g (1 mmol) of carbamate **Ie**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 241 (4.54), 289 (3.49).

4,6-Decadiyne-1,10-diyl bis-*N*-(4-nitrophenyl)carbamate (IIf) was prepared analogously to compound **IIb** from 0.25 g (1 mmol) of carbamate **Id**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 219 (4.26), 320 (4.43).

4,6-Decadiyne-1,10-diyl bis-*N*-(4-dimethylaminophenyl)carbamate (IIg). In 1 ml of pyrrolidine was dissolved 0.07 g (0.28 mmol) of carbamate **Ig** and 5 mg (0.028 mmol) of CuI. The reaction mixture was stirred for 40 min at room temperature (TLC monitoring). The reaction mixture was quenched with saturated water solution of NH₄Cl (2 ml), and the product was extracted into THF (3×5 ml). THF was partially removed in a vacuum, and the product was precipitated by 10-fold amount of water (20 ml), filtered off, and washed with water. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 266 (4.57), 311 (3.63).

7,9-Hexadecadiyne-1,16-diyl bis-*N*-phenylcarbamate (IIh) was prepared analogously to compound **IIg** from 0.245 g (1 mmol) of carbamate **IIh**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 235 (4.18), 273 (3.36) fine structure.

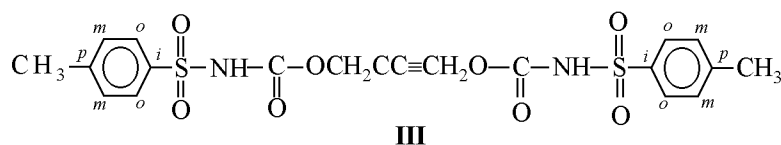
7,9-Hexadecadiyne-1,16-diyl bis-*N*-(4-dimethylaminophenyl)carbamate (IIi) was prepared analogously to compound **IIg** from 0.288 g (1 mmol) of carbamate **IIi**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 266 (4.52), 312 (3.45).

8,10-Octadecadiyne-1,18-diyl bis-*N*-phenylcarbamate (IIj) was prepared analogously to compound **IIg** from 0.2 g (0.77 mmol) of carbamate **IIj**,

15 mg (0.078 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 235 (4.41), 273 (3.40) fine structure.

10,12-Docosadiyne-1,22-diyl bis-*N*-phenylcarbamate (IIk) was prepared analogously to compound **IIg** from 0.287 g (1 mmol) of carbamate **IIk**, 19 mg (0.1 mmol) of CuI, and 1.5 ml of pyrrolidine. UV spectrum (CH₃CN), λ_{max}, nm (log ε): 235 (4.47), 273 (3.18) fine structure.

2-Butyne-1,4-diyl bis[*N,N'*-di(4-methylphenylsulfonyl)]carbamate (III) was prepared in the same way as compound **II** from 172 mg (2 mmol) of 2-butyne-1,4-diole, 0.556 ml (4 mmol) of tosyl isocyanate, 10 mg of dibutyltin bis(2-ethylhexanoate), 2 drops of Et₃N, and 5 ml of anhydrous THF. Yield 130 mg (23%), mp 166–168°C (with decomposition).



¹H NMR spectrum (CD₃COCD₃), δ, ppm: 2.43 s (6H, CH₃), 4.71 s (4H, CH₂O), 7.42 d (4H, *m*-H arom), 7.89 d (4H, *o*-H arom). ¹³C NMR spectrum (CD₃COCD₃), δ, ppm: 21.03 (CH₃), 53.62 (CH₂O) 81.16 (C≡C), 128.47 (*m*-C arom), 129.96 (*o*-C arom), 136.92 (*p*-C arom), 145.24 (*i*-C arom), 150.64 (C=O). Found, %: C 49.96; H 4.36; N 5.76. C₂₀H₂₀N₂O₈S₂. Calculated, %: C 49.99; H 4.20; N 5.83.

Polydiacetylenes IVa–k. Solid-phase topochemical polymerization of diyne carbamates **IIa–k** was carried out under UV irradiation by mercury lamps BUV-15 and PRK-400 under standard conditions for all diynes. In a weighing bottle of 58 mm diameter was charged 30 mg of diyne and 10 ml of distilled water. The weighing bottle was placed under a focusing tube connected with three low-pressure BUV-15 lamps (or under a PRK-400 lamp) at a distance of 10 cm. The irradiation was carried out for 5 min at stirring with a magnetic stirrer. Then the water was filtered off, and the weighing bottle was put into a vacuum-desiccator over P₂O₅ for 24 h. Then 5 ml of CH₂Cl₂ was added, and the precipitated polymer was filtered off. The solvent was removed in a vacuum, and the residue was weighed. With every compound two polymerization runs were performed in order to estimate the reproducibility of results. The irradiation by PRK-400 lamp was done in two modes: with and

without a Pyrex glass filter. Under the latter conditions was performed only polymerization of compounds **IIb–f, k**.

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