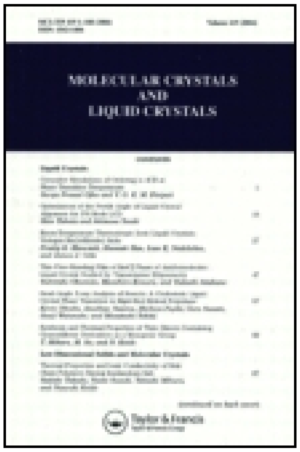

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A NOVEL SYNTHESIS OF POLYACRYLATES AND POLYMETHACRYLATES WITH PENDANT CARBAZOLE GROUPS

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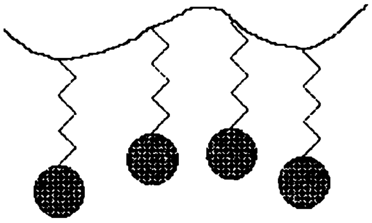
Abstract A series of novel polyacrylates and polymethacrylates with pendant carbazole groups has been prepared. In these polymers the carbazole groups are separated from the polymer backbone by alkyl spacers of variable length. The title compounds have been prepared by two different methods: free radical polymerization of the corresponding acrylates and methacrylates and a novel polymeranalogous reaction of ω-hydroxyalkylcarbazoles with poly(meth)acryloylchloride.

INTRODUCTION

Polymers with pendant carbazole groups are of interest in basic research as well as for technical applications. Since 1957 when H. Hoegl[1,2] described the photoconductivity of poly(N-vinylcarbazole) for the first time numerous polymers containing a carbazole moiety have been synthesized and investigated. Today photoconductive polymers are frequently used in photocopiers, laser printers and electrophotographic printing plates.

Although many carbazole-containing polymers have been described, there is yet no clear picture as to the correlation between the chemical structure of a polymer and its photoconductive properties. With this in mind we started the synthesis of a series of carbazole containing polymers which we use as model compounds in our investigations of the structure-property relationship.



In these polymers the nature of the main chain, the spacer and the photoconductive group can be varied systematically. Recently we have reported the synthesis[3] and photoconductive properties[4] of some novel polysiloxanes with carbazole moieties. This paper describes the synthesis of a series of polyacrylates and polymethacrylates with pendant carbazole groups.

EXPERIMENTAL PART

The preparation of the 9(ω-alkenyl)carbazoles (II) from carbazole and the corresponding ω-bromoalkenes has already been described[3].

9(6-hydroxyhexyl)carbazole (III, m = 6): In a dry 500 ml three necked flask 24.94 g 9(5-hexenyl)carbazole in 100 ml dry THF are added to a solution of 200 ml 9-Borabicyclo[3.3.1]nonan (9-BBN, 0.5 M solution in THF). The mixture is stirred for three hours at room temperature. Then 60 ml of ethanol, 20 ml 6 N NaOH and 40 ml H_2O_2 (30 %) are added subsequently and the mixture is refluxed for one hour. After the addition of 200 ml of water the THF is evaporated and the product extracted with ether. After evaporation of the solvent the product is twice recrystallized from hexane/acetone (9 : 1). 21.1 g (79 %) of white needles, m.p.: 123 °C. 9(2-hydroxyethyl)carbazole (III, m = 2), m.p.: 81 °C, Lit.: 83°C[5], 9(3-hydroxypropyl)carbazole (III, m = 3), m.p.: 98°C, 9(5-hydroxy-pentyl)carbazole (III, m = 5), m.p.: 80 °C and 9(11-hydroxyundecyl)carbazole (III, m = 11), m.p.: 76 °C were prepared in an analogous manner.

6(N-carbazolyl)hexylmethacrylate (IV, m = 6): In a dry 250 ml three necked flask 2.9 ml of methacryloylchloride in 20 ml of dry dichloromethane are added to a solution of 6.68 g 9(6-hydroxyhexyl)carbazole and 4.2 ml of triethylamine in 80 ml of dichloromethane. After stirring for three hours the reaction mixture is washed with 2 N NaOH and water. Evaporation of the solvent yields the crude product which is further purified by column chromatography with dichloromethane as eluent. Yield: 5.90 (70 %) of a colorless oil.

The other ω(N-carbazolyl)alkylacrylates and methacrylates were synthesized by the same procedure.

Poly[6(N-carbazolyl)hexylmethacrylate] (VI, m = 6) by free radical polymerization: In a 100 ml flask with nitrogen inlet 5.90 g of 6(N-carbazolyl)hexylmethacrylate and 29 mg of AIBN are dissolved in 50 ml of dry toluene. The mixture is degassed and polymerized at 60°C for 48 h. The precipitated polymer is collected and purified by two reprecipitations from chloroform solution into methanol. Yield: 5.18 g (88 %) of a white powder.

The free radical polymerization of the other acrylate and methacrylate monomers was carried out in the same way.

Poly[6(N-carbazolyl)hexylmethacrylate] (VI, m = 6) by polymeranalogous reaction: Polyacryloylchloride and polymethacryloylchloride were prepared according to a literature procedure[6].

In a flame purged 100 ml three necked flask 3.21 g of 9(6-hydroxyhexyl)carbazole in 20 ml of dry THF are added to 7.5 ml of butyl lithium (1.6 M in hexane) at 0°C. After the addition of 1.05 g of polymethacryloylchloride in 10 ml of THF the mixture is stirred for 3 hours at room temperature. The product is isolated by precipitation into methanol and purified by two reprecipitations from THF solution. Yield: 2.75 g (82 %) of a white powder.

Elemental analysis $(C_{22}H_{25}NO_2)_n$:

	C	H	N	O	Cl
calc. :	78.77	7.51	4.18	9.54	-
found:	77.56	7.40	4.29	10.40	0.41

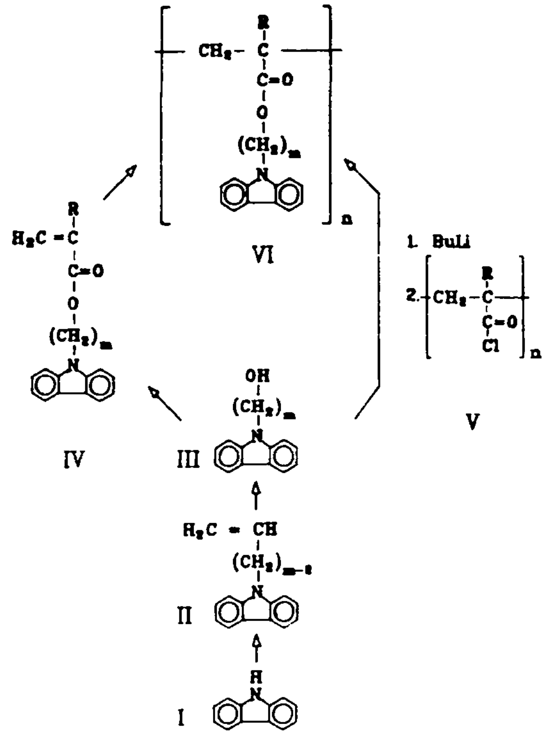
RESULTS AND DISCUSSION

A number of polymers based on the carbazole moiety have been described in the literature[7,8] since the discovery of photoconductivity in PVK. Poly[2(N-carbazolyl)ethylacrylate] and -methacrylate have been already synthesized and investigated[9-12]. Very recently, the synthesis of a number of carbazole containing polyacrylates with spacers of different length has been reported by Hu et al.[13], who used the phase transfer catalyzed reaction of 9(ω-bromoalkyl)carbazoles with sodium acrylate for the preparation of the monomers.

Free Radical Polymerization

We carried out the synthesis of a series of polyacrylates and polymethacrylates with pendant carbazole groups by two different methods which are outlined in scheme 1. In the first step of our synthesis the ω-alkenylcarbazoles II were prepared from carbazolyl-sodium and the corresponding ω-alkenylbromides[3]. Hydroboration of the olefins with 9-Borabicyclo[3.3.1]nonan (9-BBN)[14] leads to the ω(hydroxyalkyl)carbazoles III. The acrylate and methacrylate monomers were obtained by

Scheme 1:



esterification with acryloyl- and methacryloyl chloride and polymerized in toluene with AIBN as initiator. The molecular weights of the polymethacrylates are given in table I. Except for PMA 2 and PMA 6 the molecular weights are rather low and all polymers exhibit a broad molecular weight distribution. The reason for this is the low solubility of the polymers, mainly the ones with a short spacer, in the polymerization solvent toluene. In more polar solvents like THF the molecular weight is limited by chain transfer reactions.

Polymeranalogous Reaction

In many cases the polymerization of complex monomers including a variety of functional groups is difficult to obtain by classical methods like free radical, cationic or anionic polymerization. Often only oligomers or low molecular weight polymers are obtained because of side reactions of the initiator or the growing chain end with some functional groups of the monomer. The limited solubility of either monomer or polymer in the solvents required by a polymerization method also prevents the formation of high molecular weight polymers in many cases.

TABLE I: Molecular weights of the polymethacrylates VI, R = CH_3, prepared by free radical polymerization

	m	M_w a)	M_n a)
PMA 2	2	83 000	20 000
PMA 3	3	24 000	5 000
PMA 5	5	49 000	5 000
PMA 6	6	84 000	28 000
PMA 11	11	11 000	1 600

a) determined by GPC using polystyrene standards

Therefore we developed a novel polymeranalogous reaction for the synthesis of polyacrylates and polymethacrylates in which we used the highly reactive prepolymers poly(acryloylchloride) and poly(methacryloylchloride) (V). Although these polymers are known for a long time[6,15,16], there are only a few reports dealing with polymeranalogous reactions with alcohols and amines[17-21].

We have prepared poly(acryloylchloride) and poly(methacryloylchloride) by free radical polymerization of the acid chlorides according to the method of R.C. Schulz[6]. The first attempts to react poly(methacryloylchloride) with the ω-hydroxyalkylcarbazoles III showed that the esterification of the polymeric substrates proceeds very slowly compared to the low molar mass model compound pivaloyl chloride. Therefore we converted the alcohols III to the much more reactive alcoholates by means of butyl lithium. The alcoholates react much faster and the reaction, which can be easily monitored by IR-spectroscopy, is complete after a few hours at room temperature.

Polymer characterization

The IR spectra of a polymethacrylate synthesized by the two different methods are shown in Figure 1. The two spectra are almost identical. Only a very small peak at 1805 cm^{-1} (arrow) that stems from a few residual acid chloride groups can be seen in the spectrum of the polymer prepared by the novel polymeranalogous reaction. A broad absorption between 3500 and 2500 cm^{-1} is assigned to some carboxylic

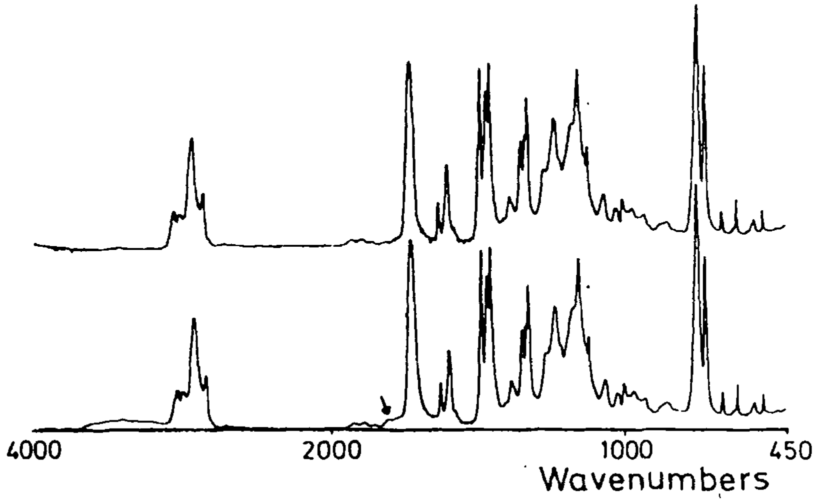


FIGURE 1 IR-spectra of poly[6 (N-carbazolyl) hexylmethacrylate] (VI, m = 6)
above: prepared by free radical polymerization
below: prepared by polymeranalogous reaction

groups in the polymer. These results are sustained by the elemental analysis (ref. experimental part). The amount of nitrogen found agrees well with the calculated one indicating that the polymeranalogous reaction yields a polymer with an almost quantitative degree of substitution. The small amount of chlorine and the deviation from the calculated oxygen value are due to some acid chloride and carboxylic groups in the polymer.

TABLE II: Glass transition temperatures of the polyacrylates and polymethacrylates prepared by polymeranalogous reaction[a)]

		2	3	5	6	11
Polyacrylates	VII, R = H	104	87	60	54	15
Polymethacrylates	VII, R = CH_3	148	113	91	73	31

a) The glass transition temperatures have been determined by DSC with a heating rate of 20 K/min

The glass transition temperatures of the polymers decrease with increasing spacer length from 148°C to 31°C for the polymethacrylates and from 104°C to 15°C for the polyacrylates. The glass transition temperatures for the polyacrylates with m = 3, 5 and 6 are somewhat higher than the values reported by Hu et al.[13], what might be a consequence of the higher molecular weights of our polymers. GPC measurements (polystyrene standards) showed that the polyacrylates had molecular weights in the range of $M_w = 10 - 15 \cdot 10^4$ and $M_n = 5 - 7 \cdot 10^4$. These values are substantially higher than the ones reported before for the polymers prepared by free radical polymerization[13].

Excellent films could be cast from the novel polyacrylates and methacrylates. Photoconductivity measurements are in progress and the results will be published in the near future.

REFERENCES

1. Ger. Pat. 1068115 (1957), Kalle AG, Invs.: H. Hoegl, O. Süs, W. Neugebauer, Chem. Abstr. 55, 20742 a (1961).
2. H. Hoegl, J. Phys. Chem. 69, 755 (1965).
3. P. Strohriegl, Makromol. Chem., Rapid Commun. 7, 771 (1986).
4. H. Domes, R. Fischer, D. Haarer, P. Strohriegl, Makromol. Chem. 190, 165 (1989).
5. R.G. Flowers, H.F. Miller, L.W. Flowers, Journ. Am. Chem. Soc. 70, 3019 (1948).
6. R.C. Schulz, P. Elzer, W. Kern, Makromol. Chem. 42, 189 (1960).
7. M. Stolka, D.M. Pai, Adv. Polym. Sci. 29, 1 (1978).
8. M. Stolka in "Encyclopedia of Polymer Science and Technology" 2nd Ed., Vol. 11, p. 154 (1988).
9. J.M. Rodriguez-Parada, V. Percec, Macromolecules 19, 55 (1986).
10. M. Keyanpour-Rad, A. Ledwith, A. Hallam, A.M. North, M. Breton, C Hoyle, J.E. Guillet, Macromolecules 11, 1114 (1978).
11. R. Oshima, T. Uryu, M. Seno, Macromolecules 18, 1045 (1985).
12. T. Uryu, H. Ohkawa, R. Oshima, Macromolecules 20, 712 (1987).
13. C.J. Hu, R. Oshima, S. Sato, M. Seno, Journ. Polym. Sci., Polym. Letters 26, 441 (1988).
14. H.C. Brown, E.F. Knights, C.G. Scouten, Journ. Am. Chem. Soc. 96, 7765 (1974).
15. S. Rondou, G. Smets, M.C. de Wilde-Delvaux, Journ. Polym. Sci. 24, 261 (1957).
16. S. Boyer, A. Rondeau, Bull. Soc. Chim. Franc. 1958, 240.
17. R.C. Schulz, P. Elzer, W. Kern, Makromol. Chem. 42, 197 (1960).
18. R.C. Schulz, P. Elzer, Makromol. Chem. 42, 205 (1960).
19. H. Kamogawa, Journ. Polym. Sci., A 1, 7, 2458 (1969).
20. I. Yahagi, M. Watanabe, K. Sanui, N. Ogata, Journ. Polym. Sci., Polym. Chem. 25, 727 (1987).
21. S. Polowinski, Acta Polymerica 35, 193 (1984).

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