Polymer Bulletin 14, 85–91 (1985)

Polymer Bulletin

Sulfur Containing Polymers

1. Copolymers of 1,3-Benzeneditiol with Phosgene and Bisphenol-A

Corrado Berti, Elisabetta Marianucci, and Francesco Pilati

Istituto Chimico, Facoltà di Ingegneria, Viale Risorgimento 2, I-40136 Bologna, Italy

SUMMARY

Copolymers containing -S-CO-S- and/or -O-CO-S- groups have been synthesized mainly by interfacial polycondensation.
Different chemical structures were obtained by reacting 1,3-benzenedithiol (BDT) respectively with phosgene alone, phosgene and bisphenol-A (BPA), bischloroformate of BPA, BPA polycarbonate oligomers and by reacting phosgene with the products of BPA polycarbonate degraded with BDT. The chemical structures of the copolymers were investigated by IR, ^{1}H-NMR and ^{13}C-NMR; molecular weights were determined by viscometry and vapor pressure osmometry. Although no attempt was made to find the optimum conditions for high molecular weight, some copolymers with fairly high mol. weight were obtained.

INTRODUCTION

It has been known for some time that sulfur-containing polymers often show excellent thermal and chemical resistence. In addition, sulfur-containing compounds are frequently mentioned in patents to be effective, alone or in mixture with other compounds, as polymer additives for thermoxidative stabilization (MAASSEN et al. 1965), flame retardants (MARK 1984), preservatives (LENHART 1984), etc.. Thus sulfur-containing polymers might be useful polymeric additives having the advantage, with respect to the low-mol. weight compounds of avoiding extraction by solvents or evaporation by heating.

Although many polymers containing sulfur have been synthesized and described in the literature, very little data are reported on the synthesis and chemical behaviour of polymers containing the oxycarbonylthio group (-O-CO-S-) (BRODE 1972, JONES and ANDREADES 1969) or the thiocarbonylthio group (-S-CO-S-) (JONES and ANDREADES 1969); we therefore decided to synthesize new polymers containing these groups.

In this paper we describe the synthesis and chemical characterization of several copolymers having different chemical structures obtained by reacting 1,3-benzenedithiol (BDT) respectively with phosgene alone, phosgene and bisphenol-A (BPA), bischloroformate of bisphenol-A (BPABCF), BPA polycarbonate oligomers and by reacting phosgene with the products of BPA polycarbonate degraded with BDT.

MATERIALS AND TECNIQUES

1,3-benzenedithiol (BDT) was an high purity Fluka product (⩾99,5%) and was used without further purification.

Gaseous phosgene (Matheson) was dissolved either in CH_2Cl_2 or in 1,1,2,2-tetrachloroethane (TCE) and stored in solution. The solution concentration was estimated by titration according to RUSH and DANNER (1948).

BPA and polycarbonate of BPA (oligomer and polymer), were kindly supplied by ENICHEM polimeri. BPABCF was synthesized according to SCHNELL and BOTTENBRUCH (1962).

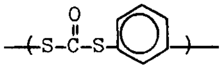
Solvents were reagent grade and were used without further purification. NMR spectra were recorded on a Varian XL-100 instrument, IR spectra were recorded on a Perkin-Elmer 257 model instrument and number-average molecular weights were obtained with a Mechrolab 310 A vapor pressure osmometer using benzil and polystyrene for calibration. Viscosity measurements were performed in Ubbelohode viscometers.

SYNTHESES AND RESULTS

The main reaction data for the different copolymers are summarized in Table 1, along with molecular weights and intrinsic viscosity. In the following we will discuss the main features of the various syntheses.

The syntheses described below were performed at room temperature in a 250 ml three necked flask equipped with a mechanical stirrer, thermometer and dropper funnel.

1 Poly(thiocarbonylthio-1,3-phenylene)



The polymer was synthesized from BDT and phosgene by both the interfacial and solution methods. The apparatus was charged with 2.63 g (18.5 mmol) of BDT, 2.8 g (70 mmol) of sodium hydroxide, 0.050 g (0.22 mmol) of benzyltriethylammonium chloride, as catalyst, 40 ml of TCE and 50 ml of water. 1.90 g (19.2 mmol) of phosgene in 62 ml of TCE were added to this mixture under vigorous stirring. After 1 h the organic phase was separated, washed once with 10% hydrochloric acid (30 ml) and twice with water. The polymer was precipitated with acetone, filtered and dried at 90°C under vacuum overnight.

As the intrinsic viscosity of the polymer obtained by the interfacial method was low, we tried to synthesize a polymer with a higher mol. weight by performing the polymerization in TCE solution (100 ml) and pyridine (6 ml) using the same amounts of reactants. The intrinsic viscosity and the polymer yield were low also in solution polymerization, as shown in Table 1; this fact can probably be attributed to a large extent of cyclization reactions.

Part of the IR spectrum of the polymer $_1$ is shown in Figure 1a. The carbonyl stretching band is at 1710 cm^{-1}, in agreement with the literature for aromatic thiocarbonates (COLTHUP et al. 1964).

NMR spectra could not be obtained owing to the low solubility of this polymer in the usual deuterated solvents. In fact, at room temperature, of the usual solvents it is soluble in TCE only.

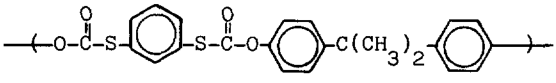
TABLE 1

Chemical and molecular characterization of copolymers

Copolymer	Reaction yield(%)	Carbonyl stretching bands (cm^{-1})	Intrinsic viscosity (dl/g)	$\overline{M}_n$ (g/mol)
1	50	1710	0.12*	/
2	95	1740	0.60**	14000
3	70	1770 1740 1710	0.08**	1200
4	95	1770 1740	0.55**	10000
5	75	1770 1740 1710	0.24**	5000

(*) in TCE at 30°C, (**) in chloroform at 30°C

2 Poly[oxycarbonylthio-1,3-phenylene-thio(carbonyl)oxy-1,4-phenylene-dimethylmethylene-1,4-phenylene]



The apparatus was charged with 0.40g (2.8 mmol) of BDT, 0.48g (12 mmol) of sodium hydroxide, 0.050g (0.22 mmol) of benzyltriethylammonium chloride, as catalyst, 40 ml of water and 30 ml of CH_2Cl_2. 0.99g (2.8 mmol) of BPABCF, dissolved in 10 ml of CH_2Cl_2, were added dropwise to the rapidly stirred system over 10 min. After 1 h of stirring the organic phase was separated, washed with 10% hydrochloric acid (10 ml) and water, and added slowly to 300 ml of methanol. The precipitated polymer was filtered and dried under vacuum at 70°C overnight.

The interfacial polymerization gave a polymer in high yield and with a fairly high mol. weight (see Table 1).

The chemical structure of the polymer was investigated by IR and NMR spectroscopy. Part of the IR spectrum is reported in Figure

1b and shows a sharp carbonyl stretching band at 1740 cm^{-1} as expected for the -O-CO-S- group (JONES and ANDREADES 1969, COLTHUP et al. 1964). ^{13}C-NMR spectrum supports a chemical structure in which each carbonyl is bonded to BDT and BPA moieties at the same time. In fact, only one peak is present in the carbonyl region (150-200 ppm), at 168 ppm, intermediate between the carbonyl peaks at 153 and 186 ppm obtained for diphenylcarbonate and S,S-diphenyl dithiocarbonate, respectively, in agreement with the datum reported by KASSIR et al. (1985). Both elemental analysis and ^{1}H-NMR spectrum are also consistent with this alternate chemical structure. In fact, a nearly 1:1 molar ratio of BPA:BDT monomeric units was calculated both from ^{1}H-NMR and from the percentage of sulfur in the polymer (see Table 2).

3 Copolymer from phosgene and an equimolar mixture of BDT and BPA.

The apparatus was charged with 1.42 g (10 mmol) of BDT,2.28 g (10 mmol) of BPA, 2.0 g (50 mmol) of sodium hydroxide, 0.050 g (0.22 mmol) of benzyltriethylammonium chloride, as catalyst, 50 ml of water and 50 ml of CH_2Cl_2. 0.28 g (2.8 mmol) of phosgene, dissolved in 50 ml of CH_2Cl_2, were added dropwise to the rapidly stirred system over 15 minutes. The mixture was vigorously stirred for 1 h. The organic phase was separated, washed with 10% hydrochloric acid (20 ml) and water,and added dropwise to 300 ml of methanol. The precipitated polymer was filtered and dried under vacuum at 70°C overnight.

A white product with a number average molecular weight of 1200 and an intrinsic viscosity of 0.08 dl/g in chloroform at 30°C was obtained. The IR spectrum (Figure 1c) shows three distinct peaks in the carbonyl stretching region at 1770, 1740 and 1710 cm^{1}, suggesting the presence of -O-CO-O, -O-CO-S- and -S-CO-S- groups in the polymer respectively. The same conclusion is supported by the ^{13}C-NMR spectrum, which shows small peaks at 153, 168 and 186 ppm. These results suggest a chemical structure with randomly distributed BPA and BDT units. The molar ratio of BPA to BDT of about 0.9, estimated by elemental analysis and by ^{1}H-NMR (see Table 2), suggests that phosgene reacts more easily with BDT than with BPA.

4 Reaction of BDT with a prepolymer of BPA polycarbonate

Oligomers of BPA polycarbonate obtained by the usual interfacial polycarbonate synthesis: [M_n = 450, intrinsic viscosity 0.05 dl/g in $CHCl_3$ and chain ended mainly by chloroformate groups, (-O-CO-Cl/-OH) = 3] were reacted by interfacial method with BDT. The apparatus was charged with 2.5 g (5.6 mmol) of polycarbonate oligomers, 0.56g (14 mmol) of sodium hydroxide, 0.050 g (0.22 mmol) of benzyltriethyl ammonium chloride, as catalyst, 50 ml of water and 35 ml of CH_2Cl_2. 0.50 g (3.5 mmol) of BDT dissolved in 15 ml of CH_2Cl_2 were added dropwise to the rapidly stirred system over 10 minutes. The mixture was stired vigorously for 1 h. The organic phase was separated, washed with 10% hydrochloric acid (20 ml) and added slowly to 300 ml of methanol. The precipitated polymer was filtered and dried

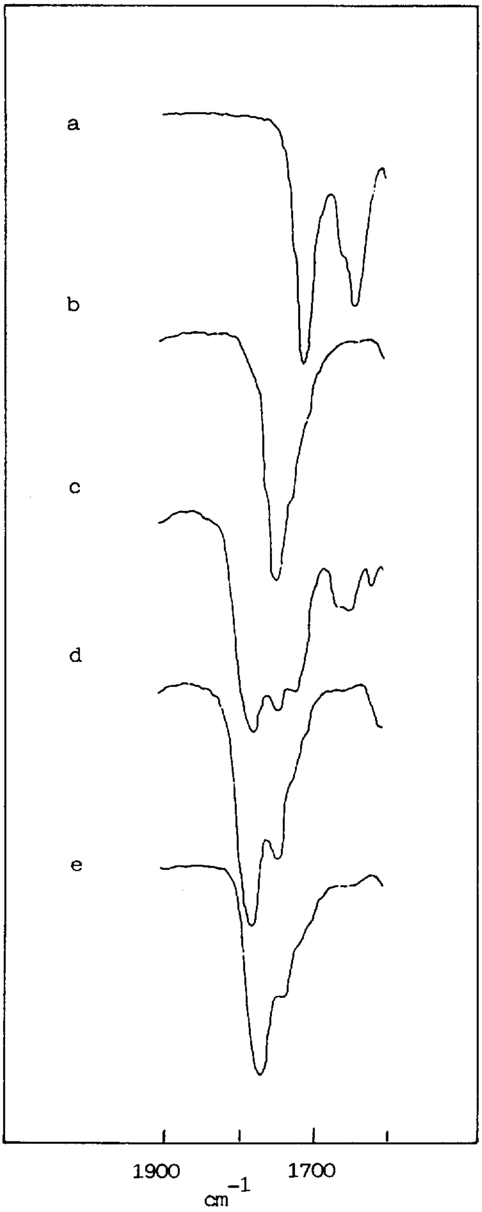


Figure 1:IR spectra of the carbonyl stretching bands of the various copolymers

in vacuum at 70°C overnight.

The intrinsic viscosity of the obtained polymer was 0.55 dl/g. The IR spectrum (Figure 1d) attests to the presence of both -O-CO-O- and -O-CO-S- groups, as does the ^{13}C-NMR spectrum. A molar ratio of BPA to BDT of about 4 (see Table 2) was estimated for the reprecipitated polymer from the elemental analysis and ^{1}H-NMR spectrum.

5 Reaction of phosgene with the products resulting from the chemical reaction of BDT with BPA polycarbonate.

A solution of 0.35g (2.5 mmol) of BDT and 0.050g (0.4 mmol) of 4-dimethylaminopyridine, as catalyst, in 5 ml of pyridine was added to a solution of 2.0g (8.8 mmol) of BPA polycarbonate in 50 ml of CH_2Cl_2 and 20 ml of pyridine. The resulting mixture was refluxed under stirring for 1 h; it was then cooled to room temperature, washed with 10% hydrochloric acid (2x100 ml) and water. The product was precipitated in acetone, filtered and dried under vacuum at 70°C overnight (1.68 g obtained). 0.44g (4.4 mmol) of phosgene in 20 ml of CH_2Cl_2 were added to the degraded polymer in the usual apparatus with 0.30g (7.5 mmol) of sodium hydroxide, 0.050g (0.22 mmol) of benzyltriethylammonium chloride, as catalyst, 50 ml of water and 50 ml of CH_2Cl_2. The mixture was stirred vigorously for 1 h. The organic phase was separated, washed with 10% hydrochloric acid (20 ml) and water, and added slowly to 300 ml of methanol. The precipitated polymer was filtered and dried in vacuum at 70°C overnight. During the degradation the intrinsic viscosity of the BPA polycarbonate decreased from an initial value of 0.75 to 0.07 dl/g, and the -O-CO-S-band appeared in the IR spectrum.

The final polymer, obtained by reacting phosgene with the polycarbonate degraded as described above, had a number average molecular weight of 5000 and an intrinsic viscosity of 0.24 dl/g in chloroform. Its chemical structure was investigated by IR (Figure 1e), ^{1}H-NMR and ^{13}C-NMR spectroscopy and was similar to that of random copolymer obtained from BDT, BPA and phosgene. The molar ratio of BPA : BDT was estimated to be about 4 by both elemental analysis and ^{1}H-NMR (see Table 2).

TABLE 2
Elemental analysis and composition data

Copol.	C%		H%		S%		BPA: BDT molar ratio	
	found	calc.	found	calc.	found	calc.	by elem. analysis	by ^{1}H-NMR
2	65.50	66.96*	4.31	4.60*	14.62	16.25*	1.1	0.9
3	62.52	64.47**	4.20	4.16**	16.44	-	0.9	0.7
4	70.70	69.60**	5.08	5.02**	5.86	-	3.6	3.4
5	70.98	71.85**	5.18	5.06**	5.44	-	4.0	3.6

* Calculated according to the alternate chemical structure

** Calculated assuming S% as correct

CONCLUSIONS

From the above results we can conclude that BDT can easily react, by the interfacial method, with phosgene or chloroformate groups to yield polymers containing -O-CO-S- and/or -S-CO-S- groups.

Different chemical structures of copolymers with BPA were synthesized from different initial conditions. It was thus possible to obtain an alternate copolymer by reacting BDT with BPABCF, whereas copolymers with BDT monomeric units randomly spaced along the chains were obtained both by reacting phosgene with a mixture of BDT and BPA and by reacting a prepolymer of BPA polycarbonate with BDT.

Although no attempt was made to find the optimum conditions for high molecular weight, some copolymers with a fairly high molecular weight were obtained.

REFERENCES

BRODE G.L. and PICKERING T.L. U.S. Patent 3, 640, 965 (1972)

COLTHUP N.B., DALY L.H. and WIBERLEY S.E.: Introduction to Infrared and Raman Spectroscopy, London, Academic Press (1964)

JONES F.N. and ANDREADES S.: J. Org. Chem. 34, 3011 (1969)

KASSIR F., BOIVIN S., BOILEAU S., CHERADAME H., WOODEN G.P. and OLOFSON R.A.: Polymer, 26, 443 (1985)
LENHART S.J.:Modern Plastics Encyclopedia 61(10A); 171 (1984)
MAASSEN G.C., FAWCETT R.J. and CONNELL W.R. in Encyclopedia of Polymer Science and Technology, New York, John Wiley and Sons, Vol. 2,171 (1965)
MARK V.:U.S.Patent 4, 430, 485 (1984)
RUSH C.A. and DANNER C.E.:Anal. Chem. 20, 644 (1948)
SCHNELL H. and BOTTENBRUCH L.:Makromol. Chem. 57, 1, (1962)

AKNOWLEDGEMENTS

We thank prof. Piero Manaresi for the useful suggestions. This work has been supported by financial aid from the Ministero della Pubblica Istruzione.

Accepted June 6, 1985 C