AUTOXIDATIVE DEGRADATION OF POLY(PHENYLACETYLENE)

Jiří VOHLÍDAL, Dana RÉDROVÁ, Marta PACOVSKÁ and Jan SEDLÁČEK
*Department of Physical and Macromolecular Chemistry,
Charles University, 128 40 Prague 2, The Czech Republic*

Received April 23, 1993
Accepted June 24, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Autoxidative degradation of high molecular-weight poly(phenylacetylene) (PPhA) in the solid state and in solution was studied using the size exclusion chromatography (SEC) and UV, IR, and EPR spectrometry. No degradation was observed on PPhA stored in vacuum, whereas the polymer exposed to air was found to degrade without any induction period. No evidence of a cross-linking of oxidized PPhA was observed. The degradation of PPhA was found to be: (i) practically non-influenced by an ambient, diffuse day-light; (ii) of the random type (i.e. each main-chain bond of PPhA has the same probability of being ruptured); and (iii) fast enough to influence the results of SEC measurements.

Although polyacetylenes visually look to be quite stable polymers, actually they are not. Even in mild, atmospheric conditions those polymers rather easily undergo the autoxidation that usually changes their key properties so deeply that they cannot further operate as active materials in photoelectronic devices, membrane separation processes[1,2], etc.

Chemistry of the autoxidation of polyacetylenes has been most in detail studied on poly(methylacetylene) and conclusions drawn from these studies are regarded as relevant also for autoxidation of other polyacetylenes (see e.g. chapter 7 ref.[1]). In contrast with polyolefins, poly(methylacetylene) is autoxidized without any observable induction period. The initiation of its autoxidative degradation is therefore supposed to proceed via a direct reaction of triplet-state oxygen with polymeric chains. The spin-prohibition of such reaction is supposed to be suppressed by a presence and/or continuous generation of neutral defects (unpaired electrons) on the conjugated main chains of those polymers. The neutral defects can be either immobile (i.e. localized) or mobile (i.e. diffusive – usually referred to as neutral solitons) and, which is important, they may be generated with a catalytic assistance of molecular oxygen[1] through its strong van der Waals interactions with long sequences of conjugated bonds.

Poly(phenylacetylene) PPhA is noncrystalline substituted polyacetylene which, in contradistinction to poly(methylacetylene), has slightly electron-withdrawing pendant groups. Difference in autoxidation reactivity of those two polymers might be thus expected. Furthermore, PPhA was shown to exhibit interesting physical properties namely the photoconductivity and nonlinear optical phenomena of the second order[3 – 6]. Thus, the knowledge of autoxidative degradation of PPhA is desirable also from this point of view.

High molecular-weight samples of PPhA can be prepared by means of metathesis polymerization[5,7,8] of phenylacetylene and their autoxidative degradation can be monitored through a decrease in molecular-weight averages of this polymer[7,9,10]. In present paper the results of study on the kinetics and mechanism of autoxidative degradation of PPhA in the solid state and in two various solvents, tetrahydrofuran (THF) and chlorobenzene (PhCl), both in a presence and absence of radical scavenger 2,6-di-*tert*-butyl-*p*-cresol (BHT) are reported. THF was chosen as the solvent which is most frequently used as a mobile phase for SEC analyses of polymers and PhCl as the solvent standardly used for autoxidation studies.

EXPERIMENTAL

Poly(phenylacetylene) was prepared by the metathesis polymerization of phenylacetylene catalyzed by $WOCl_4/2(C_6H_5)_4Sn$ in the mixed solvent benzene–1,4-dioxane[5]. Polymerization was conducted by the standard vacuum technique[7]. The precipitated and isolated PPhA was immediately dried on vacuum line (at room temperature) and then stored under the vacuum in sealed glass ampoules. All the laboratory procedures used in PPhA preparation were already described in detail[5,7].

Solvents and stabilizer. Tetrahydrofuran (THF) (Ubichem) was reduced and dried by refluxing with cuprous chloride and sodium hydride, respectively, and distilled on 45 TP column. Chlorobenzene (PhCl) (Lachema) was purified by the standard procedure[11], dried by refluxing with calcium hydride and distilled on 45 TP column. The radical scavenger 2,6-di-*tert*-butyl-*p*-cresol (BHT) (Lachema, Ionol) was used as supplied in the concentration of 2 g dm^{-3} (of the solvent).

Size exclusion chromatography (SEC). HPLC chromatograph (Laboratorní přístroje) fitted with UV-VIS detector LCD 2563 working at wavelength of 254 nm was used for SEC analyses of PPhA samples. Three columns in series packed with the following gels: (i) LI 100 (Merck), (ii) SGX 500 (Tessek), and (iii) SGX 1000 (Tessek) with integral exclusion limit from 500 to ca $3 \cdot 10^6$ (for polystyrene standards) and distilled tetrahydrofuran as a mobile phase (0.5 cm^3 min^{-1}) were used. Values of apparent molecular-weight averages based on the polystyrene standards were calculated from measured SEC curves by the routine procedure without any data correction for the axial dispersion.

Spectrometry. UV-VIS spectra of PPhA solutions were measured by PYE UNICAM SP 8-100 instrument using both standard and vacuum quartz cuvettes with optical path length of 1 mm. IR spectra were recorded using Perkin–Elmer instrument with data station 3 600 by means of KBr disk technique. Spectra EPR were recorded using ERS-220 instrument (Centre for Scientific Instruments, German Acad. Sci., Berlin) in the X-band at room temperature.

Tests of the time stability of PPhA in vacuum conditions were carried out in the following manner. In case of the solid polymer, the storage ampoules with PPhA were gradually opened, an amount of ca 5 mg of PPhA weighed to a sample vial where it was dissolved in 10 cm^3 of THF, and 15 μl of the resulting solution was injected into SEC column (the dissolution was fast – it was completed within 5 to 10 min). Only first SEC analysis of each sample was taken into account because all further analyses were considerably influenced by the degradation of PPhA in the solution. In case of the solution of PPhA, an amount of 10 mg of the polymer was dissolved in 20 cm^3 of THF using the vacuum technique and the resulting solution was distributed to vacuum storage ampoules and vacuum quartz cuvette. At given time intervals the sealed storage ampoules were gradually opened and the solution injected into SEC system immediately afterwards. Paralelly, the UV-VIS spectra of the solution in sealed quartz cuvette were recorded in time intervals from 1 to 4 days.

Autoxidation of PPhA in the solid state. An amount of ca 75 mg of PPhA was placed into covered Petri dish and stored at laboratory temperature either in the dark or exposed to the diffuse day light. At given time intervals an amount of PPhA (2 to 3 mg) was dissolved in THF (5 to 7 cm^3) and ca 15 μl of the prepared solution was immediately injected into SEC system. The time intervals between the sampling of solid PPhA were from 2 to 4 days.

Autoxidation of PPhA in solutions. A storage vacuum ampoule with PPhA was opened, amount of ca 5 mg of the polymer was weighed into a sample vial and dissolved in 10 cm^3 of pure solvent (THF of PhCl) or solution of BHT stabilizer in the respective solvent. The vial with the solution was stored either on a diffuse day-light or in the dark. An amount of 15 μl of the prepared solution was gradually sampled and injected into the SEC system.

THEORY OF RANDOM DEGRADATION OF POLYMERS

It is assumed in the model of random degradation of a polymer that the probability of rupture of a bond in any main chain depends neither on a bond position in a chain nor on the chain length, i.e. all main-chain bonds of a polymer are assumed to be equally accessible to rupture[12 - 14]. The Simha equation[14] adjusted to this model[14 - 16] is

$$\frac{dN_X}{dt} = -(X-1)\,\nu\,N_X + 2\nu\sum_{S>X}^{X_{max}} S\,N_S\,, \tag{1}$$

where N_X stands for number of molecules with degree of polymerization, (D.P.) of X, ν is the rate constant of a bond scission, and S is D.P. as the sum variable. Exact solution of Eq. (*1*) gives Eq. (*2*) which describes the time-dependence of $\langle X\rangle_n$ of randomly degrading polymer with an arbitrary initial distribution of X,

$$1/\langle X\rangle_n = 1 - (1 - 1/\langle X\rangle_{n,0})\,e^{-\nu t} \approx 1/\langle X\rangle_{n,0} + \nu t\,, \tag{2}$$

where $\langle X\rangle_{n,0}$ is a number-average D.P. at an arbitrary time $t = 0$.

The equations derived for the time-dependencies of weight-average D.P., $\langle X\rangle_w$, and z-average D.P., $\langle X\rangle_z$, are the followings[9,17],

$$\frac{1}{\langle X\rangle_w} = \frac{1}{\langle X\rangle_{w,0}} + \frac{\nu}{3}\int_0^t I_w\,dt \approx \frac{1}{\langle X\rangle_{w,0}} + \frac{\nu}{3}\,I_w\,t \tag{3}$$

$$\frac{1}{\langle X\rangle_z} = \frac{1}{\langle X\rangle_{z,0}} + \frac{\nu}{2}\int_0^t \left(I_z - \frac{2}{3}\right) \mathrm{d}t \approx \frac{1}{\langle X\rangle_{z,0}} + \frac{\nu}{2}\left(I_z - \frac{2}{3}\right) t \,, \tag{4}$$

where $\langle X\rangle_{w,0}$ and $\langle X\rangle_{z,0}$ are the values of corresponding averages of D.P. at the time $t = 0$, and $I_w = \langle X\rangle_z/\langle X\rangle_w$ and $I_z = \langle X\rangle_{z+1}/\langle X\rangle_z$ are the indexes of molecular nonuniformity related to the variance of the respective (weight- and z-) distribution function of D.P. The approximate relations with simple variable t are valid if no changes in the respective molecular nonuniformity index occur in the course of degradation. This is fulfilled if the distribution of D.P. of a starting polymer is of the Schulz–Flory type because it is known that the distribution of D.P. of any randomly degrading polymer aims at the Schulz–Flory most probable distribution function[12 - 16].

In addition to the above methods, the rate constant ν can be ascertained from SEC records by another, very simple procedure based on the dependence of the apex position of SEC peak, X_p, on time of degradation, t, providing the position of SEC peak appex is identical with that of the logarithmic distribution function, $w(\ln X)$, of a measured polymer. For a randomly degrading polymer with the initial Schulz–Flory distribution of D.P. following general equation can be derived[17],

$$1/X_p = 1/X_{p,0} + \nu t/2 \,, \tag{5}$$

where $1/X_{p,0}$ is the position of SEC peak apex at an arbitrary time $t = 0$.

RESULTS AND DISCUSSION

Stability of PPhA in Vacuum

Evidence of the long-time stability of PPhA in vacuum conditions is given in Table I. It is evident that PPhA, when kept in evacuated ampoules, remains practically intact for a period of at least two years (in the solid state) or 50 days (in THF solution). The found differences in values of molecular-weight averages are fairly within the experimental errors of SEC method. Additional proof of the stability of PPhA in vacuum was obtained from spectroscopic measurements. The UV-VIS spectrum of PPhA solution stored directly in a sealed vacuum cuvette did not alter for approximately one month (see also later). So it is obvious that PPhA, when kept under vacuum conditions does not undergo any degradation and/or changes detectable in its electronic spectrum.

Spectra EPR and IR Spectra

The autoxidation is supposed to be a process with free-radical intermediates that can be visualized by EPR spectroscopy. Spectra EPR of fresh PPhA (ca 100 mg samples) in the solid state were measured in vacuo and at atmospheric conditions too. Practically no EPR signal was observed for solid PPhA closed in vacuum cuvette. This result corresponds well to the low value of the free carrier concentration ($1.7 \cdot 10^9$ cm^{-3}) ascertained earlier[5] from the dark conductivity measurement for PPhA sample prepared in the same manner as those used in the present study. Only a weak EPR signal with $g = 2.0036$ (linewidth $\Delta H_{pp} = 13.6$ G), which is characteristic of unpaired electrons in conjugated systems[1], was found for PPhA samples exposed to atmosphere. The spectrum EPR did not alter appreciably either after the irradiation of the sample by a mercury UV lamp for 20 min or after its exposition to air for ca 1 000 h (in the latter case the sample was already considerably degraded – its molecular weight decreased to approximately one sixth of the primary value). The observed stability of unpaired spin signal might be attributed to a non-reactivity of delocalized neutral defects with re-

TABLE I

Moment characteristics of PPhA stored in vacuum in the solid state and in THF solution: t_s is the storage time, $\langle M \rangle_n$, $\langle M \rangle_w$, and $\langle M \rangle_z$ are the number-, weight-, and z-average molecular weights, respectively, and I_n, I_w, and I_z are the respective indexes of molecular non-uniformity

t_s, h	$\langle M \rangle_n \cdot 10^{-3}$	$\langle M \rangle_w \cdot 10^{-3}$	$\langle M \rangle_z \cdot 10^{-3}$	I_n	I_w	I_z
			Solid state			
0	400	860	1 380	2.15	1.60	1.30
18	365	730	1 140	2.0	1.56	1.31
330	365	725	1 190	1.99	1.63	1.33
331[a]	340	715	1 160	2.10	1.62	1.33
1 535	320	740	1 150	2.31	1.55	1.35
1 536[a]	315	715	1 120	2.27	1.56	1.29
15 000[a]	355	710	1 050	2.0	1.48	1.34
			THF solution			
10	370	750	1 200	2.03	1.60	1.39
25	365	720	1 140	1.97	1.58	1.37
75[a]	375	735	1 080	1.96	1.47	1.29
336	395	795	1 180	2.01	1.48	1.33
360[a]	365	680	1 030	1.86	1.52	1.30
1 200	355	715	1 060	2.02	1.48	1.29

[a] Sample stored in the dark place.

stricted mobility and/or to an establishing of the steady-state concentration of mobile defects through a competition between their continuous formation[1,18] and disappearance in e.g. subsequent reactions with oxygen.

IR spectra of PPhA samples degraded at various conditions are shown in Fig. 1. The spectrum of PPhA sample, which was autoxidized for 50 days in the solid state, see Fig. 1*a*, is almost identical with the already published spectrum of fresh PPhA (ref.[5]). It means that the extent of chemical changes of the PPhA sample treated in such a manner is very small. Taking into account the molecular weight of the oxidized sample ($\langle M \rangle_n$ = 60 000) and assuming both ends of each macromolecule to be chemically changed, the portion of the transformed monomeric units should be ca 0.3%. It is therefore reliable that no changes were observed either in IR or in ESR spectrum of the sample.

In contrast with the previous, remarkable changes are seen in the IR spectra of PPhA after its autoxidation for 50 days in THF or PhCl solution. It should be mentioned that the products of such autoxidation are not red or orange polymers but yellowish mixtures of oligomeric compounds only. The most important finding is the appearance of three new, strong, and broad bands in the IR spectra of those products (Figs 1*b* and 1*c*): (i) the band with maximum at 1 070 cm^{-1} which can be attributed to a presence of various ethers and/or peroxides; (ii) the band at 1 720 cm^{-1} testifying to a presence of various carbonyl groups; and (iii) the band at 3 420 cm^{-1} that can be assigned to the stretching vibrations of hydrogen bonded OH groups in alcohols and/or hydro-

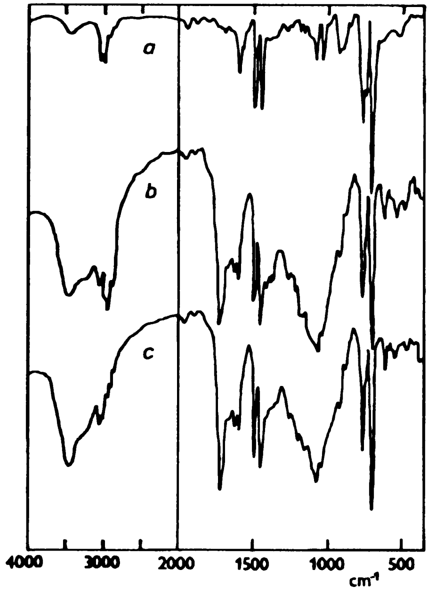

Fig. 1

IR spectra of PPhA samples autoxidized: *a* in the solid state for 50 days, *b* in THF solution for 50 days, and *c* in chlorobenzene solution for 20 days peroxides. The presence of all the mentioned groups might be considered as a serious proof of the autoxidative mechanism of the degradation of PPhA.

There are distinct bands in frequency regions from 2 850 cm^{-1} to 2 960 cm^{-1} and from 1 360 cm^{-1} to 1 420 cm^{-1} developed in the IR spectra of PPhA samples which were degraded in THF (see the spectrum in Fig. 1*b*). Those bands are characteristic of stretching and bending vibrations of aliphatic groups CH, CH_2, and CH_3. Traces of those bands are usually present in IR spectra of fresh samples of PPhA (see Fig. 1*a*) and, as it seen from Fig. 1*c*, they are also present in the IR spectrum of PPhA after its degradation in PhCl. The presence of small amounts of aliphatic groups in fresh samples of PPhA and in the polymer isolated from PhCl solution can be attributed to cyclohexadiene units[19,20] or to some other aliphatic groups formed as a minor side product during the autoxidation of the polymer. However, the aliphatic groups found in the polymer isolated from THF solution should be mostly attributed to THF units built in the highly degraded polymer. The fact that THF itself is well known to undergo the autoxidation supports this idea because intermediates of both those autoxidative processes can mutually recombine.

Changes in the UV-VIS Spectra of PPhA Exposed to Air

The UV-VIS spectra of PPhA were measured in pure THF only. They generally consist of the standard band of phenyl groups with a maximum at 254 nm and the broad band of conjugated polyene main chains. The latter band (see Fig. 2) has an inexpressive maximum of variable position (up to ca 400 nm, see Fig. 2, curve *1*) and a low-energy absorption tail that may be attributed to the low (metal) dimensionality of PPhA and/or the length distribution of conjugated sequences. Maximum of this PPhA band is blue-shifted by at least 250 nm from the *trans*-polyacetylene (maximum at 660 nm, ref.[1])

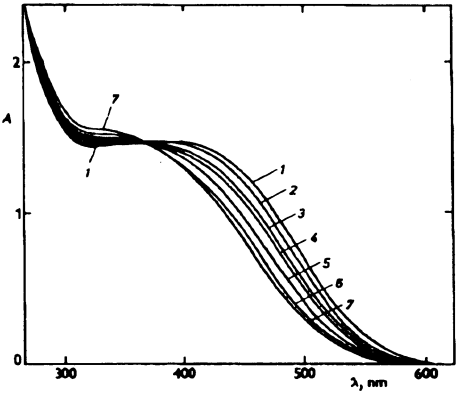

FIG. 2
UV spectra of the solution of PPhA in THF autoxidized on air for various time (in h): *1* fresh sample, *2* 4, *3* 21, *4* 28, *5* 71, *6* 145, *7* 195

obviously owing to a partial distorting of the main chain π-bonds by pendant phenyl groups.

If PPhA dissolved in THF is exposed to air, the intensity of its polyene UV band decreases continuously in the higher and, at the same time, increases in the lower wavelength region, see Fig. 2, while the band of phenyls remains intact (therefore is not included in the Fig. 2). These changes obviously reflect a transformation of longer conjugated sequences to the shorter ones – the longer conjugated sequence the higher wavelength of absorption maximum. It well corresponds to the simple idea that short conjugated sequences are being formed from the longer ones in the course of degradation as a result of the cutting of long macromolecules to the short ones. Thus the changes in UV spectra could be in principle used as a simple method for a brief, qualitative monitoring of PPhA degradation. It is clear, however, that their use for quantitative estimation of a value of the rate constant of degradation should be disputable as the changes in UV spectra of PPhA are not expressive enough for such purposes.

Kinetics of Degradation

The samples of PPhA were autoxidized in air either in the dark or on the diffuse day light: (i) in the solid state; (ii) in THF solution; (iii) in THF solution with the added radical scavenger BHT; (iv) in PhCl solution; and (v) in PhCl solution with added BHT. The measured time-dependences of D.P. of PPhA were evaluated using Eqs (*2*) to (*5*). Because the values of molecular non-uniformity indexes found for the initial samples were close to those characteristic of ideal Schulz–Flory distribution (I_n = 2.0, I_w = 1.5 and I_z = 1.33), the simplified forms of Eqs (*3*) and (*4*) were applied. Examples

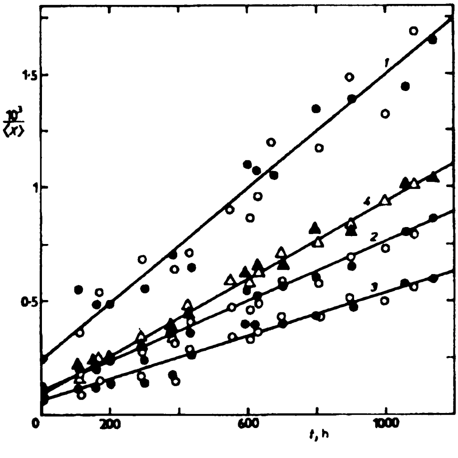

FIG. 3

Time-dependence of degree of polymerization (X) for the degradation of PPhA in the solid state in the dark (●, ▲) and at ambient diffuse light (○, Δ): *1* number-average ($\langle X \rangle_n$), *2* weight-average ($\langle X \rangle_w$), *3* z-average ($\langle X \rangle_z$), *4* reciprocal value of D.P. corresponding to the appex position of SEC peak $1/X_p$

of typical kinetic dependences for samples of PPhA degraded at various conditions are shown in Figs 3 to 6.

The kinetic dependences for PPhA samples autoxidized in the solid state are plotted in Fig. 3. Full and empty points belong to PPhA autoxidized in the dark and on ambient light, respectively. It is evident that there is practically no difference between the rates of the degradation of solid PPhA in the dark and on diffuse light. No accelerative effect of the diffuse day light was found also for the degradation of PPhA in solutions (see Figs 4 and 5). It therefore seems that the diffuse light has small, almost negligible effect on the course of autoxidative degradation of PPhA, which is rather unexpected result. However, if PPhA solution in a quartz cuvette was illuminated with an argon-ion laser (line 514.5 nm; laser power at the sample 120 mW) the dissolved polymer degraded totally within two minutes. Thus, in principle, PPhA is sensitive enough to photoxidation and the observed zero accelerative effect of the day light should be thus attributed to a low intensity of diffuse light rather than to any other reason. Therefrom follows that the "dark initiation" of the degradation via a direct reaction of oxygen with PPhA monomer units is considerably faster process than a photoinitiation under the applied reaction conditions. Therefore, the data obtained for PPhA autoxidation in the dark and on ambient light, respectively, were treated and compared with theory together.

Good linearity of all the dependences shown in Figs 3 to 6 demonstrates the random character of PPhA autoxidative degradation. Values of the rate constant ν are summarized in Table II. Good agreement of the values ascertained by different methods is evident. Deviation of an individual value from the mean one does not exceed 15% in any case.

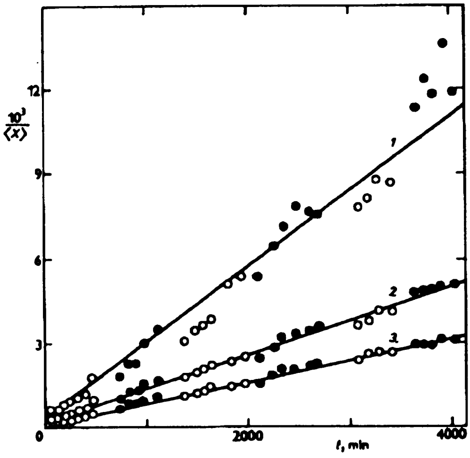

FIG. 4

Time-dependence of degree of polymerization $\langle X\rangle$ for the degradation of PPhA in THF solution: *1* number-average ($\langle X\rangle_n$), *2* weight-average ($\langle X\rangle_w$), *3* z-average ($\langle X\rangle_z$); ○ prepared solution and measured instantaneously, ● prepared solution and stored in the dark for 12 h prior to its first SEC analysis

It follows from the ascertained values of ν that the degradation of PPhA in a solution is about two orders in magnitude faster than that in the solid state. In spite of it, the degradation of PPhA in the solid state is quite fast. In the solid PPhA exposed to air the medium lifetime, τ, of a macromolecule with D.P. of about 1 000 (i.e. with the molecular weight of ca 100 000) is 27.5 days only (calculated with a use of medium value of ν of $2.5 \cdot 10^{-8}$ min^{-1}, $\tau = 1/\nu X$). It is not too much for a practical application of this polymer. If PPhA is dissolved, a stability of its "stripped" macromolecules covered by a solvate shell only is still substantially lower – the medium lifetime of a macromolecule with D.P. value of 1 000 is ca 6.5 h only, and if the macromolecule is longer, its τ can be calculated merely in minutes. For example, a macromolecule with molecular

TABLE II

Values of the rate constant of a bond rupture in a main chain of PPhA, ν (min^{-1}), found for autoxidative degradation of this polymer at various conditions at ambient room temperature. Values of ν_n, ν_w, ν_z, and ν_p were ascertained from the time-dependencies of $\langle X\rangle_n$, $\langle X\rangle_w$, $\langle X\rangle_z$, and X_p, respectively

Conditions	$\nu_n \cdot 10^6$	$\nu_w \cdot 10^6$	$\nu_z \cdot 10^6$	$\nu_p \cdot 10^6$
Solid state	0.021	0.022	0.024	0.027
THF	2.75	2.50	2.40	2.50
PhCl	4.45	4.20	4.10	4.20
THF + BHT	1.65	1.60	1.70	1.60
PhCl + BHT	1.55	1.60	1.60	1.60

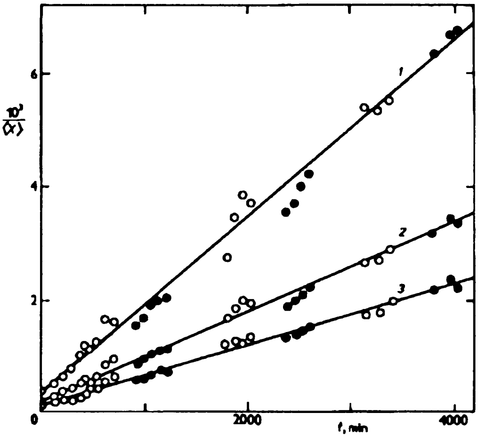

FIG. 5

Time-dependence of degree of polymerization (X) for the degradation of PPhA in PhCl solution containing BHT stabilizer: *1* number-average ($\langle X\rangle_n$), *2* weight-average ($\langle X\rangle_w$), *3* z-average ($\langle X\rangle_z$); ○ prepared solution and measured instantaneously, ● prepared solution and stored in the dark for 12 h prior to its first SEC analysis weight about 1 000 000, has the medium lifetime in THF solution ca 40 min and in PhCl solution less than 25 min only. It means that the autoxidative degradation of PPhA in a solution is so fast that it should even influence the results of SEC analyses of this polymer. Furthermore, the high rate of degradation of conjugated polyenes should be taken into account also in studies aimed to an elucidation of a relations between polymerization conditions and distribution of D.P. The original distribution of D.P. might be changed completely to the most probable one during a reprecipitation of the polymer and other procedures performed in air. It cannot be excluded that such a process also contributed to the found most probable distribution of D.P. of the starting PPhA samples used in the present study, although its reprecipitation was done under the nitrogen atmosphere.

The higher rate of PPhA degradation in PhCl in comparison with THF (by a factor 1.7) can be explained by simultaneous autoxidation of THF. This competitive reaction (to autoxidation of PPhA) should reduce a steady state concentration of oxygen in the solution and so retard the autoxidation of the dissolved PPhA. This idea is supported by the conclusions drawn from IR spectra of PPhA autoxidized in solution (see above). In contradiction with THF, chlorobenzene is known as a solvent with high power of resistance with respect to oxidation (therefore, it is often used as a solvent for autoxidation studies of polymers). Thus in this solvent macromolecules of PPhA have all the dissolved oxygen to disposal for own autoxidation.

As to the influence of the radical scavenger BHT on PPhA autoxidation, it is evident the stabilizer does not prevent the dissolved macromolecules from their autoxidative degradation (no induction period occurred at beginning of PPhA autoxidation in the presence of BHT). It is, however, seen that BHT little reduces the rate of this process. (Similar, not expressive effect of BHT on autoxidation was observed in the case of

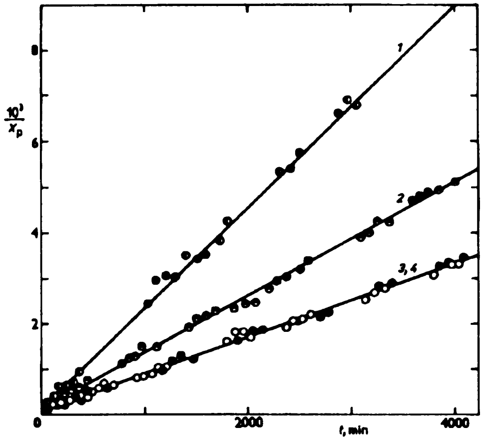

FIG. 6

Time-dependence of the reciprocal value of degree of polymerization corresponding to the appex position of SEC peak (X_p) for the degradation of PPhA in solution. Solvent: *1* PhCl, *2* THF, *3* (●) PhCl with BHT stabilizer, *4* (○) THF with BHT stabilizer poly(methylacetylene)[1], too.) It can be thus concluded that BHT presumably does not inhibit the initiation of the overall autoxidation, it only interferes with, but does not prevent, the consecutive reactions of active intermediates resulting in the rupture of main-chain bonds. The observed drop in the rate constant v to the same value $1.6 \cdot 10^{-6}$ min^{-1} for PPhA degradation in THF and PhCl caused by the addition of BHT to the respective solutions can be attributed for example to an existence of at least two possible reaction pathways to a chain rupture, of which one can whereas the other one cannot be blocked by BHT.

The authors are indebted to Dr Karel Mach from The J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, for his kind help with recording and interpretation of the EPR spectra.

REFERENCES

1. Chien J. C. W.: *Polyacetylene – Chemistry, Physics and Material Science.* Academic Press, New York 1984.
2. Masuda T., Higashimura T.: Adv. Polym. Sci. *81*, 121 (1987).
3. Kang E. T., Ehrlich P., Anderson W. A.: Mol. Cryst. Liq. Cryst. *106*, 305 (1984).
4. Kang E. T., Ehrlich P., Bhatt A. P., Anderson W. A.: Macromolecules *17*, 1020 (1984).
5. Pfleger J., Nešpůrek S., Vohlídal J.: Mol. Cryst. Liq. Cryst. *166*, 143 (1989).
6. Pfleger J.: *Ph.D. Thesis.* Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 1989.
7. Vohlídal J., Hollander A., Jančálková M., Sedláček J., Sargánková I.: Collect. Czech. Chem. Commun. *56*, 351 (1991).
8. Sedláček J., Vohlídal J., Pacovská M., Ketan P., Máca B.: Collect. Czech. Chem. Commun., in press.
9. Vohlídal J.: Presented at *34th IUPAC International Symposium on Macromolecules, Prague 1992*; Book of Abstracts, 8-P43.
10. Sedláček J., Vohlídal J., Grubisic-Gallot Z.: Makromol. Chem. Rapid. Commun. *14*, 51 (1993).
11. Riddick J. A., Bunger W. B.: *Organic Solvents, Physical Properties and Methods of Purification*, 3rd ed. Interscience, New York 1970.
12. Flory J. P.: J. Am. Chem. Soc. *58*, 1877 (1936).
13. Montroll E. W., Simha R.: J. Chem. Phys. *8*, 721 (1940).
14. Simha R.: J. Appl. Phys. *12*, 569 (1941).
15. Basedow M., Ebert K. H., Ederer H. E.: Macromolecules *11*, 774 (1978).
16. Ballauf M., Wolf B. A.: Macromolecules *14*, 654 (1981).
17. Vohlídal J.: Unpublished results.
18. Gibson H. W., Pochan J. M.: Macromolecules *15*, 242 (1982).
19. Percec V., Rinaldi P. L.: Polym. Bull. (Berlin) 9, 548 (1983).
20. Percec V.: Polym. Bull. (Berlin) *10*, 1 (1983).

Translated by the author (J. V.).