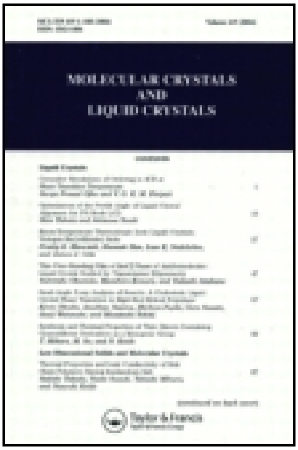

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Supramolecular Modification of Optical Properties of Some New Polyazomethines

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Supramolecular Modification of Optical Properties of Some New Polyazomethines

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Novel polyazomethines containing triphenylamine structure in the main chain have been prepared on a way of polycondensation of 4,4′-diformyltriphenylamine with aromatic diamines in HMPT solution with the goal to study interactions between polymer chain (Ps) and dopant (methanesulfonic acid: MSA, m-cresol: MC and p-chlorophenol: pClp) by FTIR, UV-vis and PL measurements. The electronic absorption spectra and photoluminescence spectra of polyazomethines detected in various solutions were dependent on the diamines structures and could be tuned by supramolecular modification via protonation or H-bond formation of imine group with the dopant. Preliminary results suggest that the polyazomethines can be blue light emitting materials.

Keywords: blue photoluminescence; H-bonds; protonation; polyazomethines

INTRODUCTION

Conjugated polymers have gained widespread interest during the last two decades, because of their useful electronic, optoelectronic, electrochemical and nonlinear optical properties. It is connected with the fact that conjugated polymers are good materials for use in various devices

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such as light emitting diodes, photovoltaics, transistors and also as flexible displays. Among the others light emitting polymers have a special interest [1]. In particular blue light emitting polymers are deemed desirable because it is generally more difficult to prepare such diodes from inorganic materials.

Among conjugated polymers, those with extended π systems involving alternating C=C and C−C bonds are predominant. This is the case of many prototypical conjugated polymers, such as polyacetylene, poly(p-phenylene) and poly(p-phenylene-vinylene). Since the C=N group is isoelectronic with the C=C group, the incorporation of nitrogen atoms into the conjugated system leads to another class of conjugated polymers closely related to poly(p-phenylene vinylene)s, namely aromatic poly(azomethine)s which are also extensively studied in recent years because of their interesting electronic and optical properties [2–5]. However, they have serious limitations for industrial applications due to their poor solubility or too high glass transition temperatures. Therefore many attempts were done to make polyazomethines processible because they seem to be good materials for optoelectronic applications. Among the others, polyazomethines bearing also triphenylamine units are very interesting because they contain in the main polymers chains nitrogen atoms in different hybridization. However it should be stressed that only few polymers exhibiting triphenylamine and imine structures in the main chains were synthesized from triphenylamine functionalized with amine groups. For example, Niu *et al.*, [6–7] described polyazomethines as hole transport materials, synthesized from 4,4′-diaminotriphenylamine and terephthalic aldehyde and glyoxal.

In contrary to the above polymers in our work polyazomethines were obtained in the reaction of 4,4′-diformyltriphenylamine with different diamines and the influence of the macromolecular chemical architecture on their properties were investigated. Additionally we will report the chemical (FTIR), and optical (UV-Vis and PL) characterizations of polyazomethines doped with methanesulfonic acid (MSA) and phenols (m-cresol: MC or p-chlorophenol: pClp).

EXPERIMENTAL

Materials

All reagents from Aldrich were used as received. m-Cresol was distilled before using. 4,4′-Diformyltriphenylamine was prepared according to the method described in the literature [8].

Polymer Synthesis

4,4′-Diformyltriphenylamine (0.25 mmol), diamine (0.25 mmol), 0.004 g of p-toluenesulfonic acid (PTS) and 5 ml of HMPT (hexamethylphosphoramide) were stirred and heated at 160°C during 6 h in a glass flask, purged with argon. After cooling the mixture was poured into 80 ml of methanol and resulting precipated was filtered and extracted (soxhlet apparatus) with hot methanol and vacuum dried.

Characterisation Techniques

The obtained compounds were characterised by the following techniques: elemental analysis (240 C Perkin-Elmer analyser), ^{1}H NMR (Varian Inova 300 Spectrometer, $CDCl_3$ solvent against TMS as an internal reference), and FTIR. Infrared spectra were acquired on a DIGILAB FTS-40A Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1} and for an accumulated 32 scans. Samples were analyzed in a form of solutions in chloroform, films after evaporating $CHCl_3$ onto potassium bromide plates and as pellets in potassium bromide. Melting point and Tg of the synthesized compounds were determined by differential scanning calorimetry (DSC) on a TA-DSC 2010 apparatus using sealed aluminium pans under nitrogen atmosphere. UV-vis absorption spectra were recorded using a Hewlett-Packard 8452 A spectrophotometer whereas the photoluminescence solution spectra were registered on a Fluorolog 3.12 Spex spectrometer with a 400 nm excitation line (450 W xenon lamp as the light source).

Protonation of Compounds

Doping of polyazomethines with MSA, MC, pClp was carried out at room temperature using chloroform as a solvent. Dopant was added to the solution of polyazomethines studied in the 1:2 mole ratio with respect to nitrogens.

RESULTS AND DISCUSSION

The molecular structures of 4 aromatic polyazomethines obtained by polycondensation are depicted in Figure 1 whereas their principal spectroscopic and molecular characteristics are collected in Table 1.

Polyazomethines can be easily dissolved in such solvents as MC, THF, DMA or chloroform. Moreover, polymers show film forming properties. Good optical quality films can be obtained by casting from solution on glass. The chemical structures of the polymers were characterized with ^{1}H NMR and FTIR spectroscopies.

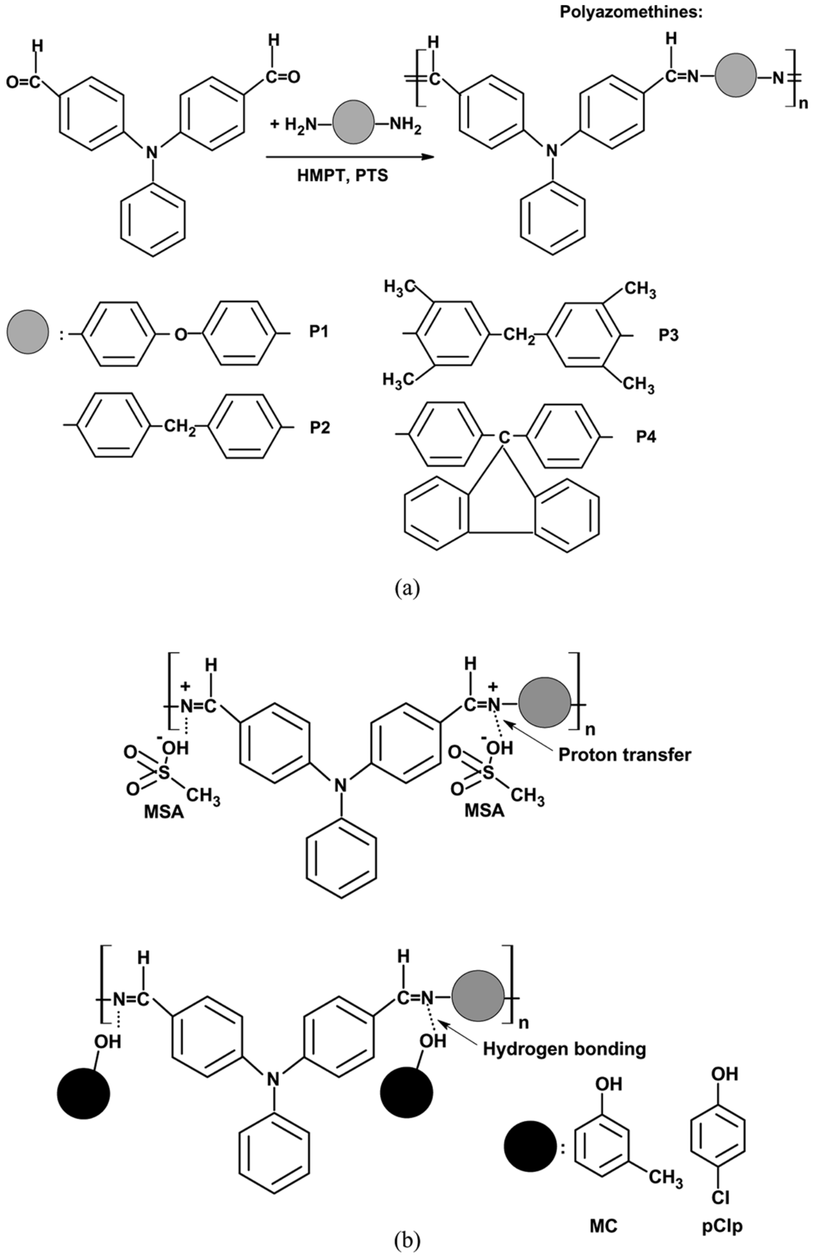

FIGURE 1 Chemical structure of synthesised compounds (a) and proposed schematic model for the interaction between the polyazomethine chains and dopant (b).

TABLE 1 Elemental Analysis, FTIR, ^{1}H NMR and DSC Characterizations of Polyazomethines

Code	Chemical Formula	Yield [%]	^{1}H NMR HC=N- [ppm]	FTIR HC=N- [cm^{-1}]	DSC, Tg [^{0}C]	Elemental Analysis Found (calculated) %N
P1	$C_{32}H_{23}N_3O_2$	50	8.42	1621	179	9.40 (9.03)
P2	$C_{33}H_{25}N_3$	60	8.39	1622	206	9.30 (9.07)
P3	$C_{37}H_{33}N_3$	40	8.15	1635	196	8.08 (8.09)
P4	$C_{45}H_{31}N_3$	56	8.40	1623	145	6.85 (7.03)

^{1}H NMR spectra consist of the signals confirming the presence of hydrogen atom in imine group, doublet at the range of 7.76–7.80 ppm due to the hydrogen atoms being at ortho position to the dialdehyde ring residue (Table 1). The other aromatic protons are confirming by multiplet in the range of 7.40–7.00 ppm. Signal at 9.85 ppm was seen in the proton NMR spectra of the polyazomethines due to the aldehyde end groups.

Furthermore, FTIR spectroscopic characterization to be presented below provides additional evidence for azomethine groups in these aromatic polyazomethines. In infrared spectra the band due to CH=N group depends on the diamine structure used for polycondensation of polyazomethines. Presence of two methyl groups at ortho position to the nitrogen atom in bis-(4-amino-3,5-dimethylphenyl)-methan causes the shift of imine stretching vibration in the polymer P3 to higher wavelength number in comparison to the other polymers studied for which the band responsible for imine group differs very little.

FTIR of Doped Polyazomethines

Therefore it seems to interesting to study how the FTIR spectra of polymer P2 and P3 will be change after protonation a lone electron pair of imine group with methanesulfonic acid (MSA) or H-bond formation with p-chlorophenol (pClp).

In the polymer P2 spectrum the band attributed to the C=N group stretching vibrations appears at 1622 cm^{-1}. After adding the metanesulphonic acid (MSA) at a ratio 1:2 this band decreases its intensity (Fig. 2). It is accompanied by appearing of the broad but low intensity band at about 1660 cm^{-1}. This indicates that the interactions of the hydrogen atom from hydroxyl group of MSA with electron pair of nitrogen from C=N group take place. In the case of the polymer P3 spectrum only slight diminishing of that band appearing at 1635 cm^{-1} is observed

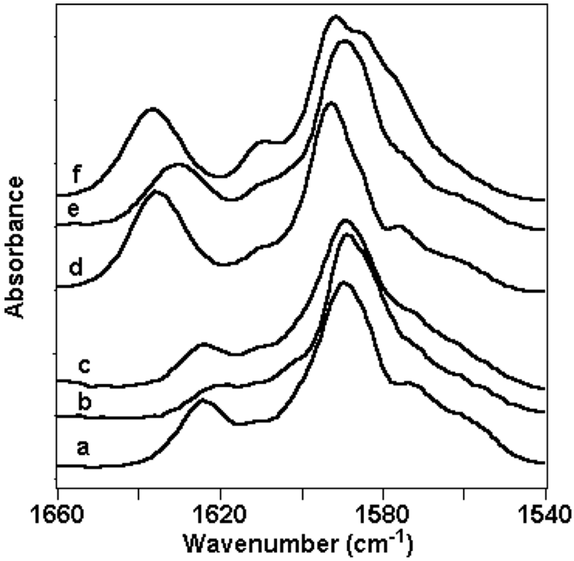

FIGURE 2 FTIR spectra of P2 (a), its mixtures at 1:2 ratio with p-Cp (b), MSA 1:2 (c), P3 (d) and its mixtures at 1:2 ratio with p-Cp (e), MSA 1:2 (f), in the region of 1660–1540 cm^{-1}.

and no new bands or shoulders appear in that region. Also in opposite to P2, for which the band supporting the forming of the N^+-H group[1–3] appears at 2630 cm^{-1}, no additional bands in that region are detected. Thus, it proves that in the case of the presence of CH_3 groups substituted to the phenyl ring in the 2,6 positions weaker interactions between C=N group and MSA are present.

However, in the case of the P3/MSA mixture some changes in the region characteristic of stretching vibrations of phenyl ring are recorded, i.e., new band at 1585 cm^{-1} with a shoulder at about 1575 cm^{-1} appears and the band at 1610 cm^{-1} becomes higher. It can suggest that some interactions between phenyl ring and MSA appear. It could be mentioned that in that region of MSA spectrum no bands are present.

Also some changes in the bands of the MSA spectrum are observed. Relatively small changes in the region of 3600–2700 cm^{-1}, characteristic for stretching vibrations of hydroxyl groups, as for the P3/MSA as P2/MSA mixtures are recorded. In the case of P2/MSA mixture intensity of a shoulder detected at 2921 cm^{-1} becomes higher in comparison to pure P2 spectrum, a new band appears at 2737 cm^{-1} and simultaneously broadening of the bands in that region is observed.

In the case of P3/MSA mixture spectrum smaller changes in relations among the bands in that region are observed.

Contrary, in the region of 1300–1100 cm^{-1} characteristic for vibrations of SO_3 group relatively higher changes are observed in the case P3/MSA mixture spectrum, i.e., besides the additional band at 1180 cm^{-1}, also high increasing of the band at 1198 cm^{-1} with a shoulder at about 1210 cm^{-1} is detected, which indicates the changes in Ph-N= group. However after adding the MSA intensity of a band at 1692 cm^{-1} ascribed to the stretching vibrations of carbonyl in the aldehyde ends groups little increases indicating possibility of hydrolysis. Similar behaviour was observed for polymer P1 and P4.

Explicit changes in the region attributed to stretching vibrations of C=N group after adding to polymers the p-chlorophenol (pClp) at the 1:2 ratio are observed. As seen from the FTIR spectra, for the both polymers P2 and P3 intensity that band diminishes more than in the case of adding the MSA and this band slightly shifts to lower wavenumber. Also in that case of these polymers the bands at 2782, 2655 and 2589 cm^{-1}, ascribed to stretching vibrations N^+-H groups appear and support the interactions between hydrogen from hydroxyl group in p-chlorophenol and nitrogen from imine.

After substracting the spectrum of pure pClp from the spectra of polymers/pClp mixtures in the region characteristic for stretching vibrations of hydroxyl groups, the broad band in the region of 3600–2500 cm^{-1} with a shoulder at about 3170 cm^{-1} is obtained. This suggests that some of OH groups interact with polymers investigated.

The changes also in the region of 1300–1200 cm^{-1} are recorded. In that region the broad band and at 1232 cm^{-1} is observed at pure pClp spectrum. At P3/pClp spectrum the bands at 1265 and a doublet at 1242 and 1229 cm^{-1} are appearing. In the case of P2/pClp mixture the band at 1229 cm^{-1} appears as a shoulder. These bands can be interpreted as deformation vibrations of phenyl ring.

Similar changes of the spectra for polymer P1 and P4 were detected. It can be said that FTIR investigations confirmed interactions of imine groups in the polyazomethines with protonation agent and H-bond donor.

UV-vis Spectroscopy of Undoped and Doped Polyazomethines

Electronic absorption spectra of the polyazomethines were detected in chloroform, dimethylacetamide (DMA) and m-cresol (MC) solutions at concentration of $1*10^{-5}$ mol/l. Solutions of the polymers in aprotic solvents (chloroform, DMA) were light yellow while in protic m-cresol were orange. Three distinct absorption bands are observed. The absorpion peak at about 270 nm is due to the transition in the aromatic ring (not show in Table 2). The absorption of the triphenylamine moiety atributed to the n-π^* transition were located in the spectral range of 340–360 nm for all polymers. The third band was located at about 380–420 nm and will be described as π-π^* transition in imine band (Table 2).

There are significant differences in the absorption bands in aprotic and protic solvents. In the aprotic solvents the absorption bands wavelengths for the certain polymers differ very little in contrary to the ones in protic m-cresol.

No influence of the linking bridge in diamines structures i.e., ether and CH_2 groups on absorption bands wavelength in the polymers P1, P2 and P4 can be seen in chloroform and DMA. However the presence of methyl substituents in the diamine in the P3 caused the blue shift of the absorption bands in these aprotic solvents in comparison with the polyazomethine P2.

The polyazomethines under investigations exhibit different behaviour in m-cresol solution. Absorption bands of the polymer with ether linkage in the chain (P1) are red shifted in protic solvent in relation to the aprotic ones. The same behaviour was observed for the polymer P3 (Table 2). The band at shorter wave side was shifted about 10 nm while the shift of the one at longer wave was equel to about 20 nm. Different changes were observed in the polymers P2 and P4 in MC solution. The absorption band at shorter wave side were 27 and 22 nm blue shifted, respectively, while the position of the band at longer wave changed very little being 3–5 nm bathochromic shifted. This seems to be due to different character of the linking bridges –ether and $-CH_2$- groups. On the other hand electrodonating methyl groups in the polymer P3 are more influencial and enforce different behaviour of this polymer in comparison with the polymer P2. This was also seen in FTIR spectroscopy.

TABLE 2 UV-vis Absorption Bands of Undoped and Doped Polyazomethines

	UV-vis, [nm]					**UV-vis in chloroform with, [nm]**		
Code	**chloroform**	**DMA**	**MC**	**film**	**Eg [eV]**	**MSA**	**MC**	**pClp**
P1	360, 401	360, 400	370, 422	360, 405	2.63	332, 387	nm	nm
P2	361, 396	361, 394	334, 399	370, 396	2.62	333, 383	361, 396	361, 396
P3	345, 383	340, 380	351, 400	340, 381	2.65	334, 383	342, 383	342, 383
P4	364, 400	nm	342, 404	nm	nm	334, 383	365, 400	365, 400

nm-not measurement.

Additionally for the azomethine films the energy gap was calculated (Table 2). The films were casted on glass plate from chloroform solution. As it is seen in Table 2 the values of Eg for all polyazomethines were comparible and were observed at about 2.63 eV.

Presence of lone electron pair in nitrogen atoms in the polyazomethines studied causes them to be sussceptible to protonation or H-bond formation with proper agents (Fig. 1b).

Protonation of imine groups in the polyazomethines with MSA in chloroform solution caused hypsochromic shift of the electronic absorption bands and their positions were almost independent of the polymer structure (Table 2). No differences in the absorption bands in UV-vis were found after adding to the chloroform solution of the polymer the H-bonding donors i.e., MC and pClp, eventhough MC used as a solvent significantly changes the electronic spectra. Probably in the last case m-cresol being in much excess influences also on polymer chains conformations along with H-bond formation and the former causes increase of conformational disorder. However it should be stressed that doping of the polymer with phenolic type species was found to enforce changes in the FTIR spectra of the polymers confirming H-bonds formation. The above relations concerned investigations carried out in proper solvents.

Photoluminescence (PL) Investigations of Undoped and Doped Polyazomethines

It is known that photoluminescence emission wavelength of polymers depend on macromolecular architecture and torsion angle of the conjugated backbons, which determines the conjugation length and the occurrence of interchain interactions [9]. On the last parameter the solvent nature and its possibility of polymer backbone solvation will influence on the photophysical properties of the polymers. In this work photoluminescence of the polyazomethines was determined in chloroform solution at concentration $1{*}10^{-4}$ mol/l and $1^{*}10^{-5}$ mol/l. It was found for undoped polymers that decrease of the concentration caused a little blue shift of the emission band of about 6 nm while intensity of photoluminescence increased several times (detected in cps). This indicates that lower concentration weaknes interchain interactions and possible aggregation. The chloroform-solution PL spectra of all undoped polyazomethines have an one emission band at about 465 nm, it means that obtained polyazomethines emitt blue light (Fig. 3a).

Effects of Bronstedt acid protonation and H-bonding formation were also investigated by PL spectroscopy. Photoluminescence of the

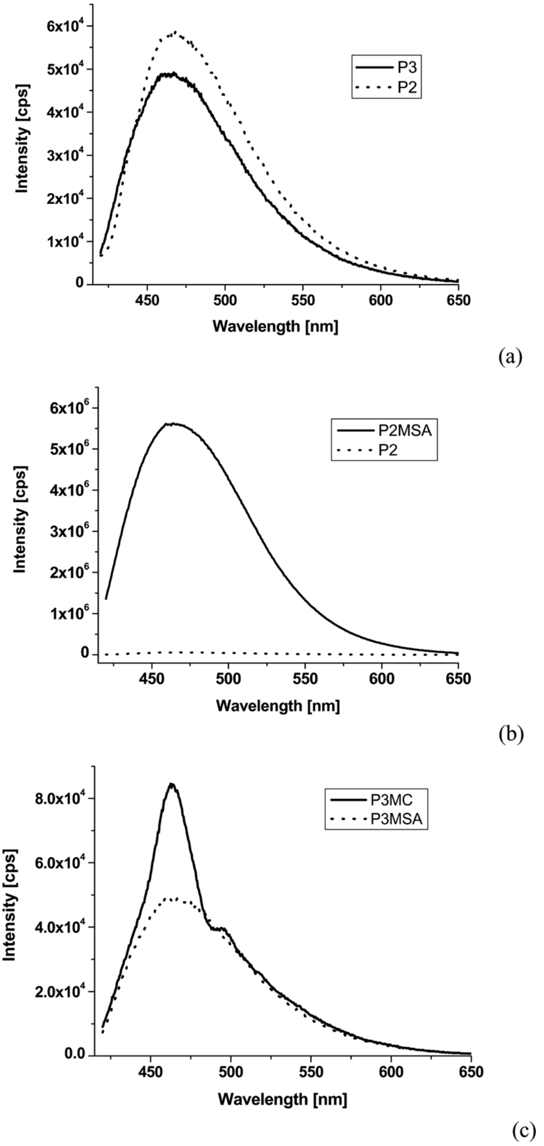

FIGURE 3 Photoluminescence spectra of the polyazomethines (a) P2, P3 in chloroform, (b) undoped and doped with MSA P2 in chloroform solution, (c) undoped and doped with MC P3 in chloroform solution. Polyazomethine:dopant in the molar ratio 1:2.

polyazomethines after addition of species that can interact with imine group was investigated at concentration $1*10^{-4}$ mol/l in chloroform solution. In the presence of MSA the emission bands of the polyazomethines were hypsochromic shifted of about 6–8 nm but the photoluminescence intensity increased significantly in orders of magnitude (Fig. 3b). Similar as in the UV-vis spectroscopy of polyazomethines doped with phenolic compounds no shift of emission wavelength was observed in the presence of phenolic type compounds i.e., m-cresol and p-chlorophenol and the band intensities were comparible with detected for the polymers in chloroform solution. Additionally, we would like to stressed that the emission spectrum of P3 doped only with MC, shows two peaks at 463 and 495 nm (Fig. 3c), which can be attributed to the 0–0 and 0–1 transitions, respectively. This part of our work is in progress.

CONCLUSIONS

In summary, we prepared a series of blue light emitting polyazomethines with triphenylamine core by the condensation of dialdehyde with various diamines. The molecular structures were identified by FTIR, NMR and elemental analysis, and the results were in accordance with the expected molecular formula.

The effect of protonating agent –MSA- and hydrogen bonding formation on the optical properties were investigated. The polyazomethines are photoactive materials and their photoluminescence was observed at about 465 nm independence of the kind of dopant and the polymer structures. Protonation was found to influence significantly on photoluminescence intensity. Study of photoluminescence yield is in progress.

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