Production of highly aligned microfiber bundles from polymethyl methacrylate via stable jet electrospinning for organic solid-state lasers

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Abstract
The fabrication of micron-sized poly(methyl methacrylate) (PMMA) polymer optical fibers doped with rhodamine B as an organic dye is demonstrated. Highly aligned and defect-free fibers are fabricated by using the stable jet electrospinning (SJES) method and systematically varying critical parameters such as solvent type and polymer concentration. At optimal conditions, for example, a polymer concentration of 35 wt% of PMMA in butanone, ribbon-shaped fibers with a smooth surface and diameter of about 20 μm could be spun using SJES mode and deposited on a rotating drum as target in a highly aligned manner. Photoluminescence spectra of the doped fibers excited longitudinally and transversely with a laser show an excitation peak with full-width-at-half-maximum of only 5.05 nm and a low lasing threshold at a pump energy of 0.55 μJ, indicating that SJES could become a new source of amplified optics components or organic solid-state fiber lasers.

KEYWORDS
fiber alignment, fiber laser, laser dye, stable-jet-electrospinning

INTRODUCTION
The first-ever organic solid-state laser (OSSL), demonstrated in 1967 by Soffer and McFarland, solved the thermal and handling problems of liquid dye lasers. Since then, efforts for the development of OSSL have increased significantly, as there are many very promising applications in the fields of medicine, sensor technology, and data communication. For lasing applications, organic dyes are an important gain material as they offer broad tuning ranges. To produce OSSL, organic dyes are typically doped into nonconjugated matrix polymers. Meanwhile, poly(methyl methacrylate) (PMMA) is a common matrix material because it provides a good transmission in the wavelength range of 400–800 nm. Different geometric forms of PMMA have been fabricated for lasing purposes, such as disk lasers, thin-film lasers,
and fiber lasers. One advantage of fiber lasers was that they could provide a certain length with a directed emission for applications. Fiber drawing or extrusion were commonly applied for the production of the corresponding fibers. In the literature of these conventional fiber laser, a spectral narrowing with a full-width-at-half-maximum (FWHM) of around 20 nm has been reported. The typical diameter for these fiber lasers was about 0.25 - 1 mm. However, for efficient lasing with much more confined FWHM, smaller diameter fibers would be beneficial according to the principle of v-number. Hence, new methods are needed to produce fibers with a diameter of only a few μm.

Electrospinning is a less studied, however promising production process for OSSL applications, as very thin continuous fibers from PMMA with diameters in the micro and nanoscale can be fabricated. Therefore, the vast majority of publications on PMMA optical fibers dealt with such nonaligned nonwoven fibers. However, it is not possible to isolate individual PMMA microfibers from these disordered fiber mats, which are profoundly desired as sensors or for optical applications. Thus, huge efforts such as utilizing rotary drum collectors or gap spinning for the generation of better-aligned fibers have been made. However, the technical applicability of fibers generated by these approaches is limited as rotating drum collectors mostly yield incomplete alignment and gap spinning is limited to small achievable fiber lengths due to limited working gap widths.

A very promising approach for upscaled generation of long and highly aligned fibers via electrospinning is the so-called stable jet electrospinning (SJES). The term was coined by Zhang et al. and describes an electrospinning process in which the chaotic whipping of the jet is suppressed. The result is a fully linear jet that yields very thin microfibers, which can be collected highly aligned on for example a rotary drum collector. Typically, bending instabilities of the jet that would lead to chaotic whipping in traditional electrospinning setups are suppressed by reducing the distance between spinneret and collector down to few centimeters. In fact, in the case of polymer melt electrospinning a whole new field of research, melt electrowriting, has emerged from this phenomenon, leading to the fabrication of highly ordered structures from electrohydrodynamic stable polymer melt jets. However, in the case of conventional electrospinning from solution, spinning at reduced spinneret-collector distance is limited due to drastically decreased drying times and collection of insufficiently dried and therefore coalesced fibers. To circumvent this problem the stable jet length can be enhanced by high viscoelasticity and chain entanglement of the polymers in the spinning solution. This can be achieved mainly by optimal polymer-solvent interactions in combination with high polymer concentration and molecular weight. It seems reasonable that the typical polymers used for OSSL application (e.g., PMMA) could be manufactured into long highly aligned microfibers via this method as well. A cheap and reliable process for the generation of such long (>few cm) fibers that could also potentially be doped with active laser dyes would have huge implications not only for OSSL applications.

Here, a novel production process for highly aligned microfibers comprised of PMMA using SJES was investigated. Systematic variations of critical parameters such as solvent choice and polymer concentration were performed and the effects of these parameters on the jet mode and the resulting fibers were studied. The fiber morphology and alignment were other major focus points of the present work. The parameters identified for optimal production of highly aligned and defect-free PMMA microfibers were subsequently applied to spinning solutions doped with different active laser dyes. From these samples, especially rhodamine B (RhB) doped fibers were studied further because the dye could be excited by a commercial green laser. Furthermore, the emission of RhB took place at a red color wavelength (around 600 nm), which could be transmitted by PMMA. Thus, optical properties such as photoluminescence spectra and lasing thresholds of the RhB doped fibers, excited longitudinally, or transversally, were measured to elicit OSSL applications of the material.

2 | MATERIALS AND METHODS

2.1 | Materials

PMMA was purchased from Röhm (Plexiglas 8N, Darmstadt, Germany) and used as obtained. Several laser dyes were investigated: 9-(2-carboxyphenyl)-6-(diethylamino)N,N-diethyl-3H-xanthen-3-iminium chloride (RhB) and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCMP) were purchased from Radiant (Wermelskirchen, Germany) while N,N′-bis(2,6-diisopropylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (perylene orange) and 3-(2-benzothiazolyl)-7-(diethylamino)coumarin (coumarin 6) were obtained from TCI.
(Tokyo, Japan) and Sigma-Aldrich (Missouri, USA), respectively. The solvents tested were obtained from different suppliers, namely dichloromethane (100%), trichloromethane (99.8%), and tetrahydrofuran (THF, 99.7%) from VWR (Pennsylvania, USA), butanone (>99%), chlorobenzene (>99.8%) and toluene (99.9%) from Sigma-Aldrich, ethyl acetate (>99.5%), and 1,4-dioxane (>99%) from ACROS (New Jersey, USA) and used without further purification.

2.2 Preparation of spinning solution

In order to successfully spin fibers from RhB doped PMMA 8 N via SJES a highly concentrated but uniform spinning solution is necessary. This was achieved by weighing appropriate amounts of polymer, dye, and solvent into a glass vial. Continuous slow stirring with a magnetic stirrer bar for more than 24 h was needed in most cases to ensure complete dissolution of PMMA. When a sample could not be dissolved after 7 days of stirring, the solvent was deemed unsuitable for our experiments. At the time of a spinning experiment, a certain amount of the resulting viscous and clear liquid was loaded into a syringe and transferred to an electrospinning apparatus for further processing.

2.3 Fabrication and characterization of electrospun fibers

The SJES process was conducted horizontally inside a custom-made chamber from acrylic glass (800 × 500 × 500 mm, 10 mm wall thickness). Two LNC-30000 high-voltage generators from Heinzinger (Rosenheim, Germany) were used to supply electrical potential. The spinneret (21-gauge needle from B. Braun Melsungen AG (Melsungen, Germany) was connected to LNC-30000 pos [positive voltage]) while a custom-made rotating drum collector (hollow aluminum cylinder with a diameter of 100 mm, length of 170 mm, and rotation frequency of 8.3–33.3 Hz, was connected to LNC-30000 neg [negative voltage]). The cylinder surface was coated with laboratory aluminum foil, which greatly improved the handling of samples after spinning. A constant flow rate of spinning solution was achieved with a syringe pump LA-30 from HLL Landgraf Laborsysteme (Langenhagen, Germany) (see Figure 1).

All scanning electron microscopy (SEM) images of fibers shown here were generated using an Evo LS 25 from Carl Zeiss Microscopy Deutschland GmbH (Oberkochen, Germany). All samples were coated with a thin gold layer using a Balzer SCD 050 Sputter coater from Leica Microsystems (Wetzlar, Germany) under argon atmosphere for 180 s at 0.42 mA before measurement in order to avoid charging effects. For determination of fiber cross-section, samples were briefly frozen in liquid nitrogen and subsequently broken at a hard surface. For analysis of fiber alignment and diameter distribution of RhB doped fiber sample, data from 40 individual specimens were manually gathered using ImageJ (Fiji).32

2.4 Measurement of photoluminescence spectra from fibers

To measure photoluminescence spectra from doped PMMA fibers, a Nd-YAG laser, purchased from Standa (Vilnius, Lithuania) with an emission wavelength of 532 nm was used. PMMA fibers doped with three different concentrations of RhB (53, 535, and 1070 ppm) were measured via longitudinal pumping and transversal pumping. Various pump energies were used for the excitation of the samples. Spectra were measured by a spectrometer (Triax 320 from HORIBA Jobin Yvon GMBH, Bensheim, Germany), which has a nitrogen-cooled CCD camera (see Figure 2).

For transversal excitation, the laser beam was focused at the side surface and near to an end of the fibers. Only 2 mm of the sample were excited. A long-pass filter was applied to remove the excitation light, so that only emission of the sample was evaluated. For longitudinally pumping, one end-surface of the fiber with a length of 50 mm was excited, while the luminescent light was measured only from the other end of the fiber. In between the fiber and the excitation source, a short-pass filter (Sp-filter) was employed which allowed passing through of the pump wavelength and reflecting
the emission of the dye back into the fiber simultaneously. For evaluation, a long-pass filter (Lp-Filter) was employed, so that only emission of the sample was detected.

3 | RESULTS AND DISCUSSION

3.1 | Identification of initial SJES process parameters

Compared to a standard electrospinning process (ES), in SJES the chaotic whipping part of the jet is eliminated.\textsuperscript{25–27} This is achieved either by reducing the distance between spinneret and collector down to few centimeters or by suppressing bending instabilities of the jet that would lead to chaotic whipping.\textsuperscript{25–28} However, in the case of conventional ES from solution, spinning at reduced spinneret-collector distance is limited due to drastically decreased drying times resulting in coalescing wet fibers.\textsuperscript{27} Another way to prevent chaotic whipping is to adjust the viscoelastic properties of the spinning solution.\textsuperscript{30,31} This can be achieved mainly by optimal polymer-solvent interactions, high polymer concentration or high molecular weight of the target polymers.\textsuperscript{31} Consequently, one approach for the manufacturing of highly aligned PMMA microfibers via SJES would be using spinning solutions with high PMMA concentration in combination with a fast rotary drum collector for the collection of parallel aligned fiber bundles. In fact, systematic variation of polymer concentration in a preliminary series of experiments at 5, 10, 15, 20, 25, 30, and 40 wt\% PMMA in THF resulted quickly in the identification of a processable concentration region (25–30 wt\%) for which stable linear jetting and collection of highly aligned fiber bundles on our setup (see Figure 3A) was observed.
Electrospray like jet behavior and no formation of a jet at all were observed below and above this region, respectively. Interestingly no typical chaotic whipping jet was observed at any of the tested PMMA concentration. Other important parameters held constant were: an applied positive voltage of +15.0 kV at the spinneret (a 21-gauge needle), a spinneret-collector distance of 300 mm, and a constant flow rate of 11 ml/h. For all experiments, the rotary drum collector was operated at the maximum speed of 33.3 Hz. This in combination with the drum diameter of 100 mm can be used to calculate circumference (314 mm) and resulting surface velocity to be 10.5 m/s. The rather high surface velocity in combination with an additionally applied negative voltage (−15.0 kV) at the collector were found to be beneficial for fiber guiding and further parallelization of the stable jet. However, the process was found to be only stable for few seconds as rapid evaporation of solvent led to subsequent drying of the Taylor cone, buildup of PMMA residue, and discontinuation of the jet (see Figure 3B). Despite this process instability, highly aligned fiber bundles with a length of approximately 300 mm were produced. It seems reasonable that reconsideration of solvent choice could resolve the encountered issue.

3.2 Consideration of optimal solvent choice for stable SJES process of PMMA

In literature, various solvents, namely dichloromethane,\textsuperscript{19} acetone,\textsuperscript{19,21} trichloromethane,\textsuperscript{13,14,19,20,33} THF,\textsuperscript{19} ethyl acetate,\textsuperscript{19} chlorobenzene,\textsuperscript{16} hexafluoro isopropanol (HFIP),\textsuperscript{18} and \textit{N},\textit{N}-dimethylformamide (DMF)\textsuperscript{15,19,33,34} have been used for fabrication of nano- or microfibers from PMMA via electrospinning. Especially Lu et al. have already compared six of the above solvents for electrospinning of a PMMA sample with $M_w$ of 500,000 g/mol at a polymer concentration of 20 wt\%.\textsuperscript{19} They were able to fabricate collapsed ribbon-shaped microfibers with porous surfaces from volatile solvents such DCM, trichloromethane, and ethyl acetate, nonporous fibers with wrinkled surfaces from THF and acetone and nanofibers with beads from DMF.\textsuperscript{19} Different solvent volatilities were used for explanation of most of these structures, while the beads in the case of DMF were attributed to too low polymer concentration for this solvent.

We, therefore, performed a series of experiments testing general processability of most of the mentioned solvents for generation of highly aligned PMMA microfibers for SJES. Because of the encountered process instability and formation of PMMA residues at the spinneret when using THF in above preliminary experiments, we also included three more solvents with lower volatility (e.g., butanone, 1,4-dioxane and toluene, see Table 1). However, DMF and HFIP were excluded from this study because of toxicity concerns. Regarding the polymer concentration of the spinning solutions, we used 25 wt\% of PMMA in all of the experiments. All other electrospinning parameters were kept constant following above preliminary experiments in THF.

For four of the eight solvents tested for electrospinning of PMMA, a SJES process resulting in the formation of highly aligned ribbon shaped microfibers was observed. The two solvents of this set with the highest volatility, namely DCM and trichloromethane, resulted in solid and uniform fibers with porous surfaces (see Figure 4A,B), while the less volatile solvents (THF, ethyl acetate, and 2-butanone) led to fibers with smooth surfaces (see Figure 4C,D). The pores were a result of phase separations that occurred during the spinning process.\textsuperscript{19,36–39} These phase separations have been described as a result of “breath figures,”\textsuperscript{39} vapor-induced phase separation,\textsuperscript{19,38} or thermally induced phase separation.\textsuperscript{36,37} In any case, water vapor due to the humidity of the atmosphere plays an inevitable role in the formation of porous fibers or pores at the fiber surfaces.\textsuperscript{38,39} All of the above mechanisms are based on the fact that the solvent evaporates from the jet, resulting in a cooling and possible water condensation on the fiber surface.\textsuperscript{36,37} Therefore, the effect is typically more pronounced with highly volatile solvents like trichloromethane or dichloromethane. Furthermore, the faster the evaporation from the shell, the less the pores are deformed during the stretching of the jet.\textsuperscript{19} Thus, we observed round pores in the case of dichloromethane (see Figure 4B), while they were more elliptical in the case of trichloromethane as solvent (see Figure 4A).

In all cases, ribbon like fibers with a dog-bone shaped cross-section were observed (see Figure 4A–D), which is a common phenomenon in electrospinning.\textsuperscript{19,39–41} Koombhongse and coworkers proposed a mechanism in which atmospheric pressure causes the skin of the fiber to collapse as the solvent in the gel core evaporates.\textsuperscript{40} Pai et al. proposed that the ribbon shape is due to buckling instabilities during polymer jet drying.\textsuperscript{41} During the evaporation of the solvent, a glassy shell may form on the surface of the gel-like core.\textsuperscript{36} Buckling is then triggered by continued evaporation of the solvent from the core, resulting in a contraction mismatch between the core and the shell. Pai et al. also demonstrated that the effect is more pronounced for thicker fibers due to the longer drying time.\textsuperscript{41}

In all but one case compiled in Table 1, the process was found to be instable with buildup of PMMA residues as depicted exemplary in Figure 3B. This was not unexpected as all of these solvents have low boiling points and corresponding high vapor pressures. From the remaining four tested solvents (all less volatile than THF), only butanone led to a typical electrospinning jet with chaotic whipping and resulted in the formation of thinner but nonaligned fibers. Beside a decreased diameter and a
random orientation, the fibers were comparable to that from THF and ethyl acetate in respect to shape of cross-sections and surface morphology (see Figure 4D). Interestingly, butanone was the only tested solvent for PMMA that did result in a stable process without any formation of PMMA residues, which could be run for extended time periods. The remaining three solvents, namely 1,4-dioxane, toluene, and chlorobenzene, did not result in the formation of any jet or fibers whatsoever.

### 3.3 Production of highly aligned PMMA fibers from butanone

From the results, it is obvious that volatility of solvents is a key factor for the formation of suitable SJES fibers for OSSL applications. From all tested solvents, butanone was the optimal candidate as it resulted in smooth and uniform fibers and in the only stable production process of the tested set of solvents. One last problem remaining

### TABLE 1 Influence of solvent choice on jet and resulting fiber morphology as well as process stability of attempted electrospinning at 25 wt% PMMA

| Solvent         | Boiling point (K) | Vapor pressure (mmHg) | Fiber morphology | Jet morphology | Process stability |
|-----------------|-------------------|-----------------------|------------------|----------------|------------------|
| Dichloromethane | 313               | 367                   | Aligned, porous  | SJES           | Instable         |
| Trichloromethane| 334               | 196                   | Aligned, porous  | SJES           | Instable         |
| Tetrahydrofuran | 339               | 133                   | Aligned, smooth  | SJES           | Instable         |
| Ethyl acetate   | 350               | 78                    | Aligned, smooth  | SJES           | Instable         |
| Butanone        | 353               | 75                    | Chaotic, smooth  | Electrospinning| Stable           |
| 1,4-dioxane     | 374               | 32                    | No fibers        | Droplet formation| No Jet          |
| Toluene         | 111               | 23                    | No fibers        | Droplet formation| No Jet          |
| Chlorobenzene   | 405               | 10                    | No fibers        | Droplet formation| No Jet          |

Abbreviations: PMMA, poly(methyl methacylate); SJES, stable jet electrospinning.

![Figure 4](https://example.com/figure4.png)  
**Figure 4** Scanning electron microscopy (SEM) images of surface morphology and cross-section (inset images) depicting exemplary fibers spun at 25 wt% poly(methyl methacrylate) (PMMA) 8 N from different solvents, namely trichloromethane (A), dichloromethane (B), tetrahydrofuran (THF) (C), butanone (D). Scale bars in main images represent 2 μm.
was the chaotic whipping of the jet and the resulting poor alignment of the fibers, when spinning at 25 wt% PMMA in butanone. Following the argumentation of Zhou et al.\textsuperscript{31} and the results from the above experiments with THF, it seemed highly probable that further enhancement of the chain entanglement in the spinning solution by increasing PMMA concentration should lead to sufficient stabilization of the jet and suppression of bending instabilities that drive chaotic whipping. In fact, a stable SJES process without any formation of polymer residue at the spinneret was achieved when the concentration of PMMA was increased to 35 wt% and the flow rate was raised to 20 ml/h. All other parameters were kept constant. The resulting fibers had the typical ribbon-shaped cross-section as observed before (see Figure 4D) and a smooth and defect-free surface (see Figure 5A,B). The fiber bundle was collected highly aligned with the majority of counted fibers ($N = 40$) within an angle distribution of $80 \pm 5^\circ$ respective to the horizontal axis of the SEM image. It is noteworthy that the actual center point of the angle distribution is only determined by the rotation of samples during SEM measurement and thus carries no further meaning. The observed narrow angle distribution is, however, demonstrating clearly the high fiber alignments achievable with our method. Moreover, the fibers had a diameter distribution of $20.6 \pm 4.1 \mu m$, measuring horizontally across the cross-section (see Figure 5C,D).

3.4 | Production of highly aligned PMMA fibers doped with different laser dyes

In order to use the fibers in an OSSL application they have to be doped with a gain material, typically an...
organic laser dye. This can be done by simply adding a sufficient amount of organic dye to the polymer solution before processing via SJES. Nevertheless, it has to be checked whether the process with its optimized parameters can be used as is, for spinning solutions that were doped with laser dyes. For exploratory reasons we tested several dyes including DCM, perylene orange, coumarin 6, and RhB at a concentration of 100 ppm in respect to mass of PMMA. At least for these four dyes no significant changes in the stability of the SJES process or the fiber morphology was observed. Figure 5E shows the resulting well-aligned fiber bundles and the respective spinning solutions doped with the different dyes. From a macroscopic perspective, the gain material was homogeneously distributed in the fiber bundles. This was further evidenced via light microscopy as no inhomogeneities could be observed in the fibers. During the light microscopy observation, it was noticed that there were bright spots at the end of the fibers or at cracks stemming from the handling of samples. This indicates that the electrospun PMMA showed light guiding. Therefore, the samples have potential for the application in the field of waveguiding and optics. In further experiments, we focused mainly on the laser dye RhB, as it could be exited via a commercial green laser and is also commonly applied for OSSL applications.\(^6,10,11,42\) We produced fibers doped with RhB concentrations ranging from 1–2140 ppm in respect to PMMA to identify best gain concentrations for efficient photoluminescence as well as lasing threshold. These fiber samples were produced successfully without changes to above SJES parameters, indicating again a reliable and reproducible process.

### 3.5 | Photoluminescence properties of RhB doped PMMA fibers

From fibers doped with various RhB concentrations, ranging from 1 to 2140 ppm, samples with a RhB concentration of 535 ppm were identified as optimal for further experiments, as significant reduction of FWHM emission spectra was apparent in photoluminescence measurements. Figure 6 shows the spectra of such a sample doped with 535 ppm of RhB under longitudinal and transversal excitation at different pump energies.

For longitudinally excitation, the smallest FWHM was found to be 6.55 nm at a pump energy of 64.39 \(\mu\)J and a center wavelength of 604 nm. At higher pump energies the FWHM broadened again. On the other hand, for transversally excited samples at 2.59 \(\mu\)J, the smallest FWHM achieved was 5.05 nm, while the center wavelength was found at 598 nm. Compared to transversal pumping, it is obvious that much more energy was needed to obtain the smallest FWHM for longitudinal pumping. On top of that, there was a distinct red-shift of center wavelength by using longitudinal excitation. This can be understood, using Kramers-Kronig relation, which explains that the optical properties can be changed at high illumination.\(^43\) The energy density of the longitudinal excitation was much higher than the transversal excitation. Under the longitudinal experiment setup, the pump energy was concentrated at a small area, which resulted in a high energy density. Eventually, the samples were stressed by the heat caused by high pump energy. This led to apparent changes of optical properties. The red-shift probably represents an increase of the refractive index due to the Kramers–Kronig relation.\(^43\)

To further demonstrate the lasing properties, the concentration of RhB dye was varied. Fibers with three different concentrations have been used for this purpose: 53, 535, and 1070 ppm. The pump energy was set to 64.39 \(\mu\)J for longitudinal and transversal pumping, respectively, since the smallest FWHM were observed at these settings. The results are shown in Figure 7.

Experiments with longitudinal excitation showed that the peak wavelength was shifted to higher and lower wavelengths depending on increasing or decreasing RhB concentration, respectively (see Figure 7A). A sample doped with 53 ppm RhB, was found to have a smaller peak wavelength at 593 nm compared to the peak at 604 nm described above for samples with RhB concentration of 535 ppm. At a RhB concentration of 1070 ppm, the peak wavelength was further shifted to 623 nm. Overall, a red-shift of 30 nm from the peak wavelength was detected. At higher concentrations reabsorption by RhB molecules was more likely. The reemission of the reabsorbed photons resulted in the red shift shown.\(^44\) Figure 7B shows the spectra when the samples transversely excited at 2.59 \(\mu\)J with different concentrations. Samples doped with 53 ppm RhB had a relatively wide FWHM of 42.75 nm, which might be due to too few dye molecules for the generation of a lasing. However, fibers doped with 535 ppm RhB were found to have a FWHM of 5.05 nm, which was the smallest of all samples tested. To our knowledge, this is also the smallest FWHM reported to date for aligned fiber lasers. When the RhB concentration was further increased to 1070 ppm, several peaks were observed, most likely caused by aggregates of the dye molecules. Thus, only the sample doped with 535 ppm was suitable for transversal excitation and showed the smallest FWHM.

Another important criterion for a laser is to reach a laser threshold above which the emission intensity increases significantly more with energy. A low lasing threshold is highly desirable as less energy is required for
laser activation. The lasing threshold of all three samples was determined and is shown in Figure 8.

Pumping the sample longitudinally, the lasing threshold decreased with increasing RhB concentration (see Figure 8A). At a RhB concentration of 53 ppm, a lasing threshold of 5.70 μJ was detected. The lasing threshold was reduced to 4.52 μJ when the RhB concentration was increased to 535 ppm. The sample doped with 1070 ppm RhB had a lasing threshold of 3.35 μJ. Moreover, it was observed that the slope of the curve beyond the threshold increases with increasing RhB concentration. In the case of transverse excitation, the lasing threshold was identified only for dye concentrations of 535 and 1070 ppm, which both were found at around 0.55 μJ (see Figure 8B).

No lasing threshold could be determined for the sample doped with 53 ppm RhB, as no change in the slope was detected. This indicates that no lasing state was reached at the lowest dye concentration. It can be deduced that lasing phenomena in transverse excitation can only be observed above a certain dye concentration.

In summary, it was established that for PMMA fibers produced by SJES with RhB as dye, both a reduction in the FWHM and a laser threshold could be demonstrated. Both depend on the concentration of the dye in the fiber. It was demonstrated that SJES can produce highly aligned fiber bundles which can be used as OSSL. These samples are promising candidates for further development in optical platforms, since only raw, as spun, fibers...
were investigated. For example, further drawing the fibers by heating them above the glass transition temperature of PMMA could result in even thinner fibers and reduced propagation losses. In addition, an optical cladding process could drastically improve light transition and provide a lasing spectrum with a fine FWHM for further applications as OSSL.

4 | CONCLUSION

In conclusion, we demonstrated that polymer concentration and solvent volatility are important factors for the fabrication of PMMA microfibers with defect-free and smooth surfaces by SJES. In this respect, butanone was identified as an optimal solvent for the fabrication of aligned fiber bundles of PMMA for organic solid-state fiber lasers (OSSL). Narrowing of FWHM and a clear lasing threshold were found, thus lasing was demonstrated. Besides, the lasing state was confirmed as the lasing properties can be affected by varying the dye concentration. Using PMMA fibers doped with 535 ppm RhB, an OSS fiber laser was realized. At transverse pumping, the fibers showed a FWHM of only 5.05 nm, which to our knowledge is the smallest FWHM described so far for a fiber laser.

ACKNOWLEDGMENTS

We thank Simone Schulze, ICTV TU Braunschweig for SEM measurements. Henrik-Alexander Christ and Pen Yao Ang would like to thank Henrike Ehrhorn for throwing a great farewell party that connected us and sparked the idea for this project. Henrik-Alexander Christ and Pen Yao Ang contributed equally. Open Access funding enabled and organized by Projekt DEAL.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

REFERENCES

[1] B. B. McFarland, *Appl. Phys. Lett.* 1967, 10, 208.
[2] (a) E. T. Knobbe, B. Dunn, P. D. Fuqua, F. Nishida, *Appl. Opt.* 1990, 29, 2729. (b) B. Dunn, J. I. Zink, *J. Mater. Chem.* 1991, 1, 903. (c) B. S. Dunn, J. D. Mackenzie, J. I. Zink, in *Sol-Gel Optics*, Proc. SPIE, Vol. 1328, SPIE, Bellingham 1990. (d) J. C. Altman, R. E. Stone, B. Dunn, F. Nishida, *IEEE Photonics Technol. Lett.* 1991, 3, 189. (e) F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Andersson, Q. Pei, A. J. Heeger, *Science* 1996, 273, 1833. (f) N. Tessler, G. J. Denton, R. H. Friend, *Nature* 1996, 382, 695. (g) M. Berggren, A. Dodabalapur, R. E. Slusher, *Appl. Phys. Lett.* 1997, 71, 2230. (h) T. Riedl, T. Rabe, H.-H. Johannes, W. Kowalsky, J. Wang, T. Weimann, P. Hinze, B. Nehls, T. Farrell, U. Scherf, *Appl. Phys. Lett.* 2006, 88, 241116.
[3] R. M. Ahmed, *Int. J. Photoenergy* 2009, 2009, 1.
[4] D. P. Pacheco, W. H. Russell, H. R. Aldag, in *Laser-Induced Damage in Optical Materials: 2003* (Eds: R. Scheps, H. J. Hoffmann), Vol. 5273. SPIE, Bellingham 2004.
[5] (a) S. Yuyama, T. Nakajima, K. Yamashita, K. Oe, *Appl. Phys. Lett.* 2008, 93, 23306. (b) O. Mhibik, T. Leang, A. Siove, S. Forget, S. Chénais, *Appl. Phys. Lett.* 2013, 102, 41112.
[6] K. Kuriki, T. Kobayashi, N. Imai, T. Tamura, Y. Koike, Y. Okamoto, *Polyim. Adv. Technol.* 2000, 11, 612.
[7] H. Y. Liu, H. B. Liu, G. D. Peng, P. L. Chu, *Opt. Commun.* 2006, 266, 132.
